NASA CR-54-433

Development of Improved Polymeric Materials for Cryogenic Propellant Tank Liners and Positive Expulsion Bladders

by

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Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Contract NAS 3-4183

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Falls Church, Virginia

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NASA CR- 54-433

FINAL REPORT

1 May 1964 to 30 April, 1965

DEVELOPMENT OF IMPROVED POLYMERIC MATERIALS FOR CRYOGENIC PROPELLANT TANK LINERS AND POSITIVE EXPULSION BLADDERS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

June 1965

Contract NAS 3-4183

Technical Management
NASA-Lewis Research Center
Cleveland, Ohio
Chemical Rockets Systems Division
R. F. Lark

Melpar, Inc.,
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Falls Church, Virginia

FOREWORD

This report has been prepared by the Research Division of Melpar, Inc., a subsidiary of Westinghouse Air Brake Company. The work covered herein was carried out under Contract NAS 3-4183, "Development of Improved Polymeric Materials for Cryogenic Propellant Tank Liners and Positive Expulsion Bladders." The technical work was administered by the Liquid Rocket Technology Branch of the Chemical Rocket Systems Division of NASA-Lewis Research Center. The Project Officer was Mr. R. F. Lark.

This report covers the work accomplished during the period 1 May 1964 to April 1965.

DEVELOPMENT OF IMPROVED POLYMERIC MATERIALS FOR CRYOGENIC PROPELLANT TANK LINERS AND POSITIVE EXPULSION BLADDERS

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ABSTRACT

The influence of biaxial orientation parameters on the folding endurance (twist-flex life), tensile properties, thermal expansion coefficient and permeability of poly(ethylene terephthalate) (PET) films at ambient temperature and at liquid nitrogen temperature (-196°C) was studied.

Sequential and simultaneous biaxial orientation procedures were evaluated in regard to their effect on the properties of PET films.

The twist-flex life and tensile properties of various commercial films such as Mylar types A, C, and T, Lexan, Vitel types VMF-414 and VFR-338, Kapton (H-film) and Kodar were determined at ambient temperature and at liquid nitrogen temperature.

The twist-flex method of determining the relative flexibilities of polymeric films for use in cryogenic positive expulsion bladders was studied and the important parameters affecting the results of this test were defined.

The utility of broad-line nuclear magnetic resonance as a diagnostic screening tool for assessing the potential flexibility of polymers for cryogenic applications was determined.

Non-commercially available polymers were synthesized, and their conversion into thin biaxially oriented films was studied.

Author

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SUMMARY

In order to develop improved polymeric materials for cryogenic filament wound propellant tank liners and positive expulsion bladders a research program was carried out that involved polymer synthesis, polymer characterization, fabrication of amorphous sheet, biaxial orientation and heat-setting of films, twist-flex testing of films, measurement of other physical and mechanical properties of films, and studies on the utility of broad-line NMR as a screening tool for assessing the cryogenic flexibility of polymeric materials.

It was found that Mylar T is superior to Mylar C and all other films examined to date in twist-flex life to failure at liquid nitrogen temperature (-195°C). In addition, the stretch ratio used when biaxially orienting poly (ethylene terephthalate) films has a profound effect on the twist-flex life of these films at -195°C.

Poly (ethylene isophthalate) and poly (2,6-dimethyl phenylene oxide) films show promise as candidate materials for cryogenic applications.

Broad-line NMR spectroscopy was found not to be a valid method for assessing the flexibility of a polymer below its Tg.

1. INTRODUCTION

This is the Final Report for Contract No. NAS3-4183. The purpose of this program was to develop improved polymeric materials for cryogenic filament wound propellant tank liners and positive expulsion bladders.

1.1 Background Information

Prior to the work carried out under this program the effort to develop polymeric materials for cryogenic propellant tank liners and expulsion bladders was largely applied and in brief, the effort consisted of testing various commercially available materials.

The principal goal was that of selecting polymeric films having high cryogenic folding endurance ratings as determined by cryogenic positive expulsion and simulated folding tests. The most promising material appeared to be Mylar[2] whose Tg is about 70° C. Toward the latter stages of this program, the effort was shifted to fibrous polymeric structures such as Nomex Nylon paper[3] and Dacron[4] felt. These materials were considerably more flexible at cryogenic temperatures than polymeric films but they are very permeable to gaseous and liquid cryogenic propellants. Attempts were made to employ laminates and coatings to reduce permeability. It was found that the cryogenic folding endurance of these combinations was no better than that of the weakest or least flexible component, i.e., the laminating material or coating.

Another approach was to employ unbonded multiple plys of the film of interest, most generally that of Mylar. This resulted in greater twist-flex endurance particularly at liquid nitrogen temperature. However, during flexing, permeability to cryogens appears to increase with resultant interply penetration. Single ply Mylar films though possessing promising flexibility at liquid hydrogen temperature are marginal at liquid hydrogen temperature. Though Mylar should be sufficiently flexible in liquid oxygen (LOX), since LOX temperatures are comparable to LN_2 temperature, it fails to meet the ABMA LOX impact test (which is taken as a measure of its compatibility with LOX). Teflon FEP, KEL-F, and other fluorocarbon polymers are unsatisfactory because of their low flexibility at LOX temperatures. Their use as liners is limited by the mis-match of their thermal coefficients of contraction with that of the filament wound glass reinforced plastic (epoxy) tank, in addition to possible problems in their bonding to the tank wall.

In view of the above, NASA-Lewis Research Center initiated a program wherein major emphasis would be placed on a more basic materials study effort.

1.2 Program Outline and Emphasis

During the past year Melpar together with Dr. R. Deanin of DeBell and Richardson, Inc., and Prof. E. Rochow at Harvard University as subcontractors carried out a research program that involved the following areas of work: polymer synthesis, polymer characterization, fabrication of amorphous sheet, biaxial orientation and heat-setting of films, twist-flex testing of films, measurement of other physical and mechanical properties of films, and studies on the utility of broad-line NMR as a screening tool.

Major emphasis in this program was placed on polymers of the aromatic polyester type since previous testing (refer to section 1.1) had shown that Mylar A and C were superior to all other commercially available polymeric film materials for cryogenic applications.

Also of prime concern was a study of the effect of biaxial orientation on the mechanical properties of films at cryogenic temperatures.

1.3 Program Accomplishments

As a result of this program, the following information was developed.

a. Mylar T is superior to Mylar C and all other polymeric films examined to date in twist-flex life to failure at liquid nitrogen temperature (-195°C). Specifically, the twist-flex life of Mylar T is greater than 350 cycles to failure while that of Mylar C is 75 cycles to failure (employing 4 in. x 4 in. 1/2-mil films). Mylar T is believed to be a post stretched form of Mylar in the machine direction.

b. The twist-flex method of determining film performance during flexing at -195°C was evaluated. The influence of film size on twist-flex life and the reproducibility of such tests were determined. It was found that more reliable comparisons between different films can be made when 4 in. x 4 in. film specimens are used rather than 4 in. x 11 in. specimens.

c. The stretch ratio used when biaxially orienting poly (ethylene terephthalate) (PET) films has a profound effect on the twist-flex life of the film at -195°C. The temperature at which a film is stretched also influences the twist-flex life of the film at -195°C. Specifically, PET films stretched at either 3.5 x 3.5 or 4 x 4 at about 170°F have a substantially higher twist-flex endurance than those stretched 2 x 2. When PET films are stretched 3.5 x 3.5 at about 200°F their twist-flex endurance is substantially less than are the twist-flex endurances of PET films stretched 3.5 x 3.5 at about 170°F.

d. Heat-setting of PET films after stretching appears to have little if any influence on the twist-flex life of these films at -195°C. In

addition, the stretch rate used in orienting PET films does not appear to have an influence on their twist-flex life. Specifically, rates of stretch of 0.5 inches per minute and 8.0 inches per minute had no discernible influence on the twist-flex life of PET films.

e. PET films stretched 4 x 4 at about 170°F are superior to Mylar C in twist-flex life at liquid nitrogen temperature. Samples may perform comparably with Mylar T at this temperature but not enough material was available to establish this.

f. Solvent cast films (0.7 - 1.5 mils) prepared from poly (2,6-dimethyl phenylene oxide) (PPO) resin (obtained from the General Electric Co.) show fair twist-flex performance at -195°C and warrant further study.

g. Poly (ethylene isophthalate) can be formed into good amorphous films which can be biaxially oriented 4 x 4.

h. Commercial Mylar types T and C films are not uniform in regard to permeability to nitrogen and hydrogen gas at ambient temperature. At -195°C the permeability of these gases through all the films tested, commercial and experimental, was very low.

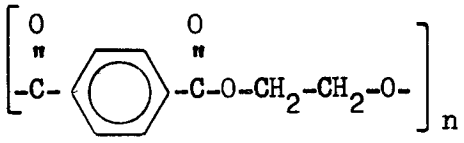
i. The use of broad-line NMR spectroscopy was found not to be a valid method for assessing the flexibility of a polymer below its T_g.

2. DISCUSSION

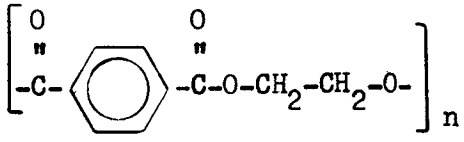
2.1 Polymer Syntheses

2.1.1 Aromatic Polyesters Via Transesterification

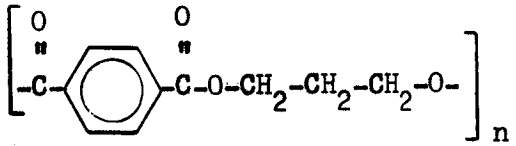
In an attempt to determine the effect of polymer structure on the cryogenic properties of aromatic polyesters of the Mylar family the synthesis of the following polyesters in 200 gram quantities was undertaken. The intent here, was to prepare the polymer resins, melt press the resins to obtain amorphous or nearly amorphous films, orient and heat-set the films and study their cryogenic properties.



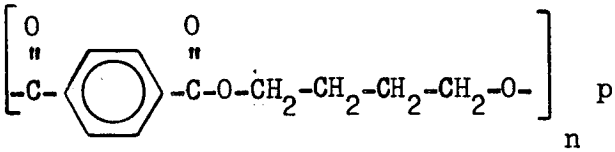
poly(ethylene terephthalate)



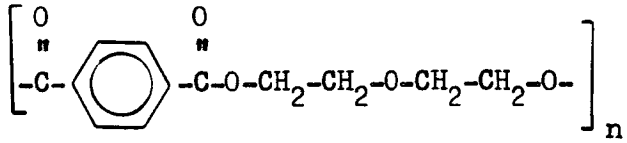
poly(ethylene isophthalate)



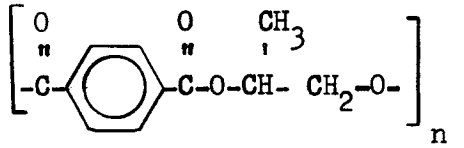
poly(trimethylene terephthalate)



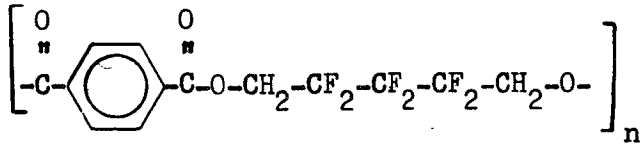
poly(tetramethylene terephthalate)



poly(diethyleneoxy terephthalate)



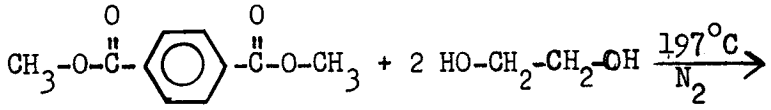
poly(1,2-propylene terephthalate)

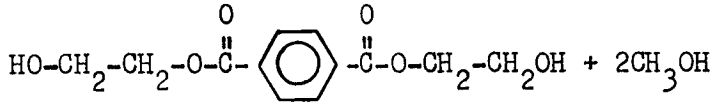


Poly(2,2,3,3,4,4,-hexafluoropentamethylene terephthalate)

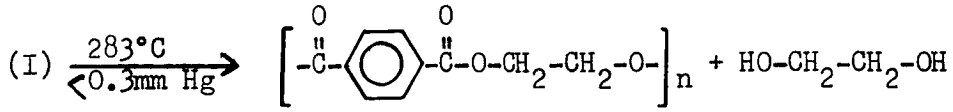
The most convenient method available for the synthesis of these aromatic polyesters involves transesterifying the dimethyl ester of the dicarboxylic acid with the appropriate glycol. This reaction is illustrated with dimethyl terephthalate and ethylene glycol.

The first step involves transesterification of dimethyl terephthalate with ethylene glycol during which methanol is removed and the prepolymer (I) is formed. The second step involves polymerization of the prepolymer during which excess ethylene glycol is removed and high polymer is formed.





(I)



A number of catalyst systems have been used in preparing polyesters by the ester interchange reaction. Calcium acetate + antimony oxide, zinc acetate, various lead salts and various titanium salts have all been reported as suitable for this type of reaction wherein high molecular weight polymer is desired.[6]

Conventional reaction conditions for PET include maintaining the reactants at an initial temperature of 195-200°C for 3 hours under nitrogen during which methanol distills out followed by a reaction temperature of 220-225°C for 0.5 hours to complete removal of methanol and start the polymerization reaction. The final polymerization is effected at 280-285°C under high vacuum ($<$0.3 mm of Hg) for three hours.

In synthesizing the above indicated polyesters of the Mylar family it was found that the procedure[6], described for poly(ethylene terephthalate) does not yield high polymers for all of the poly(methylene terephthalates). It was found that the following procedure gave high molecular weight poly(methylene terephthalates) with 3, 4, 5, and 6 methylene groups in the glycol. In brief, the procedure involves reacting dimethyl terephthalate and the appropriate glycol in a mole ratio of 1/2.1 respectively in the presence of zinc acetate dihydrate (0.19 g) and antimony trioxide (0.05 g) (Catalyst quantities are in grams per mole of dimethyl terephthalate). Nitrogen is bubbled through the reaction mixture which is maintained in a boiling ethylene glycol bath (197°C) for 20 hours to insure complete removal of methanol. The reactor is next transferred to a boiling diphenyl ether bath (259°C) and vacuum gradually applied over a 20-30 minute period. The ultimate pressure should be 0.2 mm of Hg or less. As polymerization proceeds and the glycol distills out, the melt viscosity increases rapidly. Visual

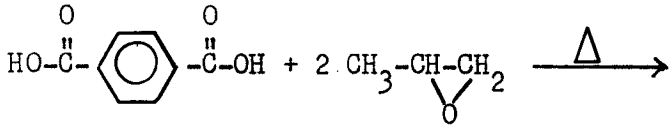
observation can be used to determine the point at which to stop the reaction since the bubbles of nitrogen have difficulty in escaping from the molten polymer, when polymer of high molecular weight has been produced. Usually this situation occurs in 5 to 10 hours.

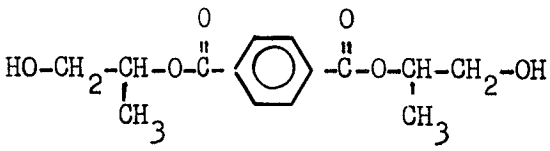
Shown in figure 1 are the polyesters prepared in this way and some of their properties, together with some of the properties measured on Mylar types A, C and T and Kodar. Two interesting observations have been made.

a. Poly(diethylene oxy terephthalate) was found to exhibit elastomeric (rubberlike) properties.

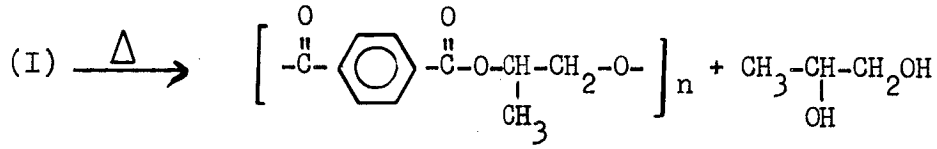
b. Poly(2,2,3,3,4,4-hexafluoropentamethylene terephthalate) was inadvertently found to be a good adhesive for glass. This was discovered when a flask coated with the resin was accidently smashed; all of the shattered pieces were held intact by the resin.

Attempts to prepare poly(1,2-propylene terephthalate) by a variety of transesterification reactions were all unsuccessful. A search of the literature indicated that this polymer has not been reported as a product of the transesterification method of polymerization. It has been reported[7] however that if the prepolymer (I) is prepared by the reaction of propylene oxide and terephthalic acid this prepolymer can subsequently be polymerized to high polymer, as shown below.

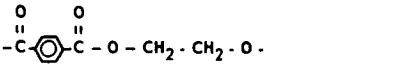
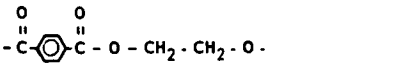
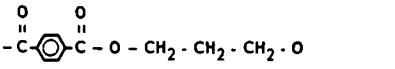
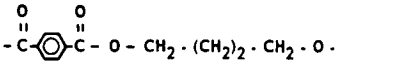
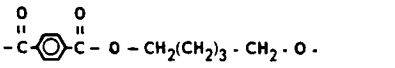
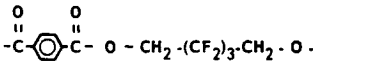
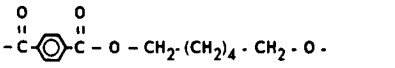
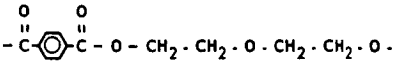
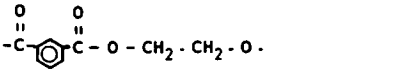
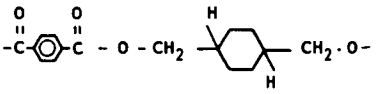




(I)



Several attempts were made to prepare poly(1,2-propylene terephthalate) by this technique but the highest inherent viscosity value obtainable was only 0.3. This was measured in a 60/40 phenol-sym. tetrachloroethane solvent as a 0.5% solution at 30°C.

POLYMER	REPEAT UNIT	INHERENT VISCOSITY	MELTING POINT OBSERVED (°C)	MELTING POINT LITERATURE[1]	DTA → DATA(5) T_g(°C)	DTA → DATA(5) T_m (°C)
POLY(ETHYLENE TEREPHTHALATE)		0.5[2]	256-64	262	69	256
MYLAR-TYPE A, C AND T (PET)		0.5[2]	———	———	—	—
POLY(TRIMETHYLENE TEREPHTHALATE)		0.5[2]	228-32	232	35	227
POLY(TETRAMETHYLENE TEREPHTHALATE)		0.5[2]	233-39	224	25	221
POLY(PENTAMETHYLENE TEREPHTHALATE)		0.6[2]	134-45	135	10	134
POLY(2,2,3,3,4,4-HEXAFLUOROPENTAMETHYLENE TEREPHTHALATE)		0.2[2]	122-28	——	—	—
POLY(HEXAMETHYLENE TEREPHTHALATE)		0.6[2]	156-161	154	-4	148
POLY(DIETHYLENE GLYCOL TEREPHTHALATE)		0.5[2]	50-58	——	—	—
POLY(ETHYLENE ISOPHTHALATE)		0.7[3]	133-35 (SOFTENS 110°)	240(6) (SOFTENS 110°)	—	—
POLY(DIMETHYLENE CYCLOHEXYLENE TEREPHTHALATE) "KODAR"		0.7[2]	295-303	295(4)	82	291

(1) A. CONIX AND R. VAN KERPEL, J. POLYMER SCI., XI, 521(1959)
(2) MEASURED IN 60/40 PHENOL-SYM-TETRACHLOROETHANE AS 0.5% SOLUTION AT 30°C.
(3) MEASURED IN O-CHLOROPHENOL AS 0.5% SOLUTION AT 30°C.
(4) EASTMAN-KODAK TECHNICAL BULLETIN
(5) SCHULKEN ET AL, ACS POLYMER PREPRINTS, 5, (NO. 2) 453 - 458 (SEPT. 1963)
(6) CRYSTALLINE MELTING POINT

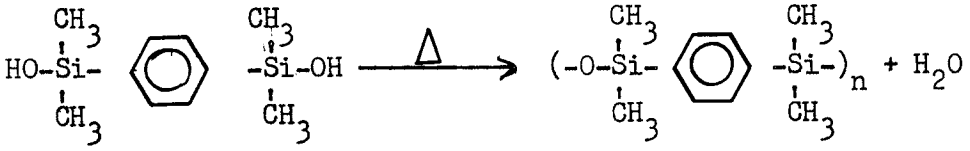
Figure 1. Polyesters and Some of Their Properties

2.1.2 Aromatic Polyesters Via Diacid Chloride-Diol Reaction

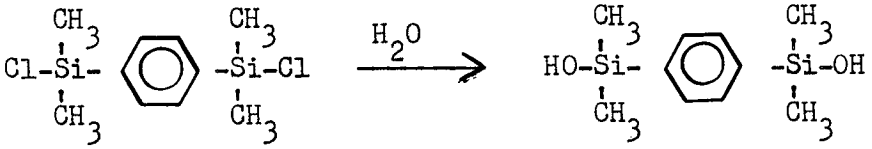
Samples of poly(1,4-phenylene terephthalate) and poly(1,4-phenylene isophthalate) were prepared by reacting the corresponding diacid chloride with hydroquinone in ortho dichlorobenzene at reflux (180°C). The procedure used was as follows: To 200 ml of o-dichlorobenzene in a 3-neck 500 ml round bottom flask equipped with a reflux condenser, nitrogen bubbler and thermometer was added 21.6 g. of hydroquinone (recrystallized from water) and 40.g. of the diacid chloride (recrystallized from heptane). Nitrogen was bubbled through the mixture at reflux until the evolution of HCl had ceased. This took 3 hours for the terephthaloyl chloride reaction and 4 hours for the isophthaloyl chloride reaction. In each case excess toluene was added to the hot solution to precipitate the polymer. The polymers were filtered and washed with heptane and vacuum oven dried at 60-80°C. Attempted melting point determinations showed that these polymers did not melt up to 360°C. Neither polymer was soluble in tetrachloroethane-phenol solvent at temperatures up to 100°C; thus inherent viscosity values could not be determined.

2.1.3 Synthesis of Poly(1,4-phenylene bis (dimethyl siloxane))

This polymer was prepared in small quantity by polymerizing the diol in the presence of aqueous sodium hydroxide as shown in the following equation:



The inherent viscosity value of this polymer was 0.7 determined in toluene at 25°C. The diol was obtained by hydrolysis of the corresponding dichloride as shown in the following equation:



The dichloride was obtained from the General Electric Company.

2.1.4 Synthesis of Kilogram Quantities of Polyesters

At about the three-quarter point of this program it was found that additional quantities (more than the original 200 gram samples) would be required to study the fabrication parameters of some of the above polyesters.

Emphasis was placed on preparing approximately one kilogram each of the C_2, C_3 and C_4 poly(methylene terephthalates) and also poly(ethylene isophthalate). Scale-up of the polymers described in sections 2.1.2 and 2.1.3 was not investigated.

The procedure used in preparing about one kilogram of each of the polyesters is illustrated below for poly(tetramethylene terephthalate). To a 2 liter, 2-neck round bottom flask equipped with a hollow shaft stirrer driven by a constant torque motor were added 950 ml of 1,4 butanediol (redistilled), 970 g. dimethyl terephthalate (Eastman Kodak, white label), 0.95 g zinc acetate hydrate (Fisher reagent grade) and 0.29 g. antimony trioxide (B and A reagent). Nitrogen was passed through the mixture via the hollow shaft stirrer. The mixture was heated to 185°C and kept at this temperature overnight with nitrogen bubbling through the stirred reaction mixture to allow complete removal of methanol. After twenty hours, vacuum was slowly applied and the temperature raised to between 240°C - 250°C. After 1.25 hours at this temperature the melt viscosity was such that the reaction was deemed complete. After cooling under nitrogen the inherent viscosity of the polymer was found to be 0.65 (tetrachloroethane-phenol, 30°C, 0.5% solution). The yield of polymer from this run was 1040 grams.

In similar fashion approximately one kilogram each of poly(ethylene terephthalate), poly(ethylene isophthalate) and poly(trimethylene terephthalate) was prepared. Inherent viscosity values for each of these polymers was 0.5 or greater.

2.1.5 Polymer Molecular Weight Measurements

In determining molecular weights of polymeric materials a value which is an average of the molecular weights of the molecules present is obtained. Osmometry gives a number average while light scattering and the ultracentrifuge give weight average molecular weights. These methods are the ultimate basis for the use of dilute solution viscosity measurements which are so widely used for determining molecular weights of synthetic polymers.

Of the various viscosity numbers commonly measured inherent viscosity values are often used and were thus chosen for use in this program. The magnitude of the inherent viscosity values of various polymer systems have been related to the resultant mechanical properties of the polymer in the fabricated end item. Although these values are common knowledge to those working in the field of polymers they are listed here for the benefit of those who have no familarity with polymer chemistry.

For the polymers listed below the inherent viscosity values given are considered minimum for the polymer to be fabricatable into articles with good tensile properties.

Polymer	Inherent Viscosity
Vinyls	0.9
Polyamides	0.8
Polyesters	0.5
Polyurethanes	0.4
Polyureas	0.4

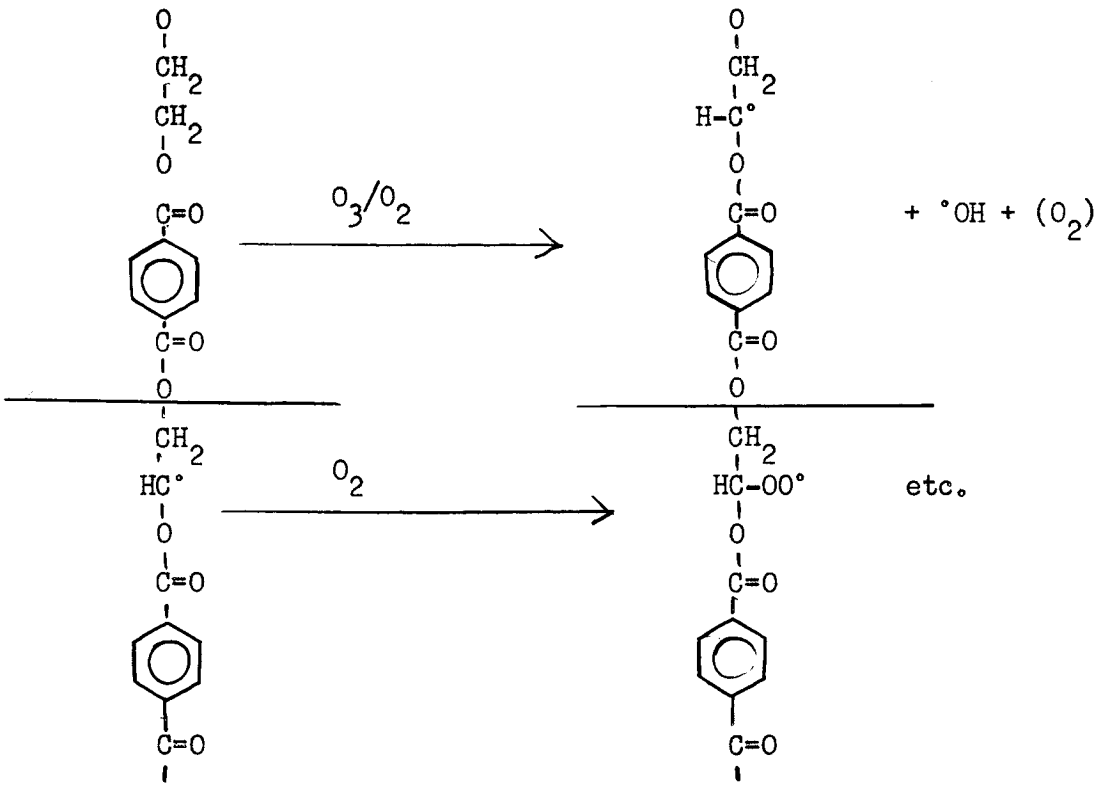
2.2 Graft Copolymerization Studies

To take advantage of both the flexibility of Mylar at liquid nitrogen temperature and the oxidative resistance of the fluorocarbons, an attempt was made to graft polymerize a fluorocarbon monomer such as chlorotrifluoroethylene on to a Mylar film substrate. The intent here was to protect Mylar film, by a fluorocarbon coating chemically bonded to the film, against attack by LOX and thus have a serviceable bladder and/or liner material for LOX.

Still another aim of the graft copolymer work was to reduce the permeability of Mylar to hydrogen for liner applications. This would involve graft copolymerizing poly (vinyl acetate) on to Mylar and alcoholysis of the acetate to give poly (vinyl alcohol) chemically bonded coating on Mylar film.

2.2.1 Graft Copolymerization Via Surface Activation by Ozone

Surface activation of the film surface was accomplished by treatment with ozone as shown in the following sequence of reactions.



Vinyl acetate monomer was used as a model compound for the fluorocarbon monomers, and also as the precursor of the poly (vinyl alcohol) mentioned above.

It was found that ozonization of Mylar at a temperature of at least 85-95°C for 3-5 hours was required before the film would initiate vinyl acetate polymerization. At this temperature films with up to 45% poly (vinyl acetate) on them were prepared. Ozonization of Mylar 1/2-mil type A at 125°C for 5 hours, however, resulted in complete degradation of the film into a tacky solid with no strength properties remaining. Investigation of the poly (vinyl acetate) coating on Mylar described above showed it to be a physical coating rather than a chemically bonded graft copolymer. The evidence for this was as follows. Infrared analysis of the benzene-free coating (removed from the Mylar by solution in benzene) disclosed that:

a. This material had all the absorption bands of poly (vinyl acetate) with an additional small absorption band at 13.7μ.

b. Poly(ethylene terephthalate) has a strong absorption band at 13.7μ.

c. Rerunning poly(vinyl acetate) homopolymer with a thicker sample specimen to yield a more intense spectrum disclosed that the homopolymer still had a weak absorption band at 13.7μ. Thus the weak band at 13.7μ in the poly(vinyl acetate) coating on Mylar was not due to a poly(ethylene terephthalate) graft copolymer with poly(vinyl acetate).

In addition, it was found that when ozonized Mylar film was placed in 10 times the amount of vinyl acetate monomer very little if any weight gain was observed on the Mylar, whereas a 45% weight gain had been observed with the smaller amount of monomer. It was thus indicated that the Mylar film adsorbed a fixed amount of ozone which was able to catalyze the polymerization of vinyl acetate to yield a fixed amount of polymer. With the use of a smaller amount of monomer, a higher concentration of polymer in monomer was achieved, and when the Mylar was removed from the monomer and dried, the film retained enough polymer (from the monomer solution) to show the weight gain. However, in the case where a larger amount of monomer was used, the resultant concentration of polymer in monomer was relatively low. In this case, when the Mylar was removed from the monomer and dried, the film retained very little if any polymer (from the monomer solution) and thus showed little if any weight gain.

2.2.2 Graft Copolymerization with Surface Activation by Irradiation.

Another mode of activating polymers for subsequent monomer polymerization is through γ-ray irradiation (Cs 137). Irradiation was carried out at room temperature in the presence of air with the aim of introducing active peroxide and/or hydroperoxide sites on the film. These sites would then be available for initiating vinyl monomer polymerization. It was found

that these irradiated films did initiate vinyl acetate polymerization and that the total dosage was important in determining the amount of vinyl acetate that was subsequently polymerized. This data is presented below.

Cesium -137 Irradiation of Mylar 1/2 Mil Type A

Irradiation at Room Temperature in Air

Vinyl Acetate Polymerization at 70°C Under Nitrogen for 4-5 Hours

Sample (No.)	Irradiation Time (Hrs)	Dosage (Megarads)	Weight change Due to Irradiation (wt %)	Weight Gain Due to Poly(vinyl acetate) on Mylar Film (wt %)
1	117.1	23.4	+0.4	6.3
2	163.2	32.7	+0.9	5.9
3	258.2	51.6	-0.1	77.5
4	306.2	61.2	+0.5	1.8
5	354.1	70.8	+0.2	0.5

It can be seen that the amount of poly(vinyl acetate) on the Mylar reached a sharp maximum at about 50 megarads dosage and fell off sharply thereafter. The bonding present in these poly(vinyl acetate) on Mylar films, however, was shown to be physical rather than chemical by treatment with benzene at room temperature. This treatment completely removed the poly(vinyl acetate) indicating that only homopolymer had been formed in the polymerization process. The reason for this homopolymer rather than graft copolymer formation observed in these experiments is not readily discernible. A possible reason could be a facile chain transfer step from growing polymer to monomer. In this case the growing polymer chain would terminate by chain transfer to monomer before appreciable graft copolymer formation could occur.

2.3 Fabrication Studies

2.3.1 Background Information

The properties of Mylar film depend very markedly upon its thermal and mechanical history and resulting morphology.[8] Above 260°C it melts to a fluid liquid. When it is cooled slowly below its melting point, it crystallizes into a mass of microscopic crystalline regions with a density of 1.455, in which the ethylene groups have a trans configuration;[8] some workers have claimed to approach 100% crystallinity by holding the polymer for many hours just below its melting point.[9] Such melting and crystallization are reversible equilibria. The fully crystallized Mylar is rigid and brittle.

On the other hand, if molten Mylar is cooled suddenly to below its glass transition temperature, it freezes to an amorphous glass of density 1.335, in which the molecules are shaped like random coils, and most of the ethylene groups have gauche configuration.[8] Such fully amorphous Mylar is somewhat soft but quite weak and brittle.

If amorphous Mylar is heated between its glass transition (70°C) and melting temperature (263°C), the molecules tend to flex into trans configuration and fold into crystals, the rate of crystallization increasing with temperature.[8] This is an irreversible change, and does not improve flexibility or toughness. It can only be reversed by the indirect path of melting and quenching again.

If amorphous Mylar is heated above its glass transition temperature, optimally 80-110°C, and stretched several hundred percent, the amorphous molecules tend to become aligned into a parallel trans conformation, assuming a fairly regular structure.[8] While some crystallization does occur, as indicated by an increase in density to about 1.36, most of the molecules simply become fairly ordered without actually reaching crystalline regularity.[8] Such orientation produces most of the flexibility and toughness for which Mylar is noted. When fibers are stretched in one direction, Dacron is produced (a uniaxial orientation). When film is stretched in two directions, Mylar is produced (a biaxial orientation). It is easy to visualize the orientation of parallel molecules in Dacron fiber, but there is still some vagueness and difficulty in visualizing the orientation of molecules in biaxially-stretched Mylar film. Biaxial orientation results in an isotropic uniplanar orientation of the molecules.

In the production of Mylar A and C, after stretching, the oriented film is heated briefly to a higher temperature, such as 10 seconds/200°C, to cause some further crystallization or heat-setting.[8] During this heat treatment, the film is restrained under tension to prevent the oriented amorphous trans conformation from elastic retraction into the unoriented amorphous gauche conformation.[8] The heat-setting presumably converts some of the

amorphous phase into crystalline phase, fastening the structure more permanently into the oriented structure which has just been produced, and thus making it more stable toward temperature and time. The increase in density to about 1.39 indicates a total crystallinity of about 40%. It is in this form that Mylar film proved so promising in earlier NASA supported studies on cryogenic flexibility.[1]

Commercial biaxial orientation is performed via a two-step operation. The film heated above its glass transition temperature is first drawn over rolls rotating at different speeds where stretching occurs about 3.5X in the machine direction. Partially oriented film is then seized by two rows of tenter frame clamps along its travelling edges, and these two rows are gradually moved farther apart to stretch the film about 3.5X in the transverse direction. Control of temperature, rate of stretching, and degree of stretching are reported to be very critical, and many patents[10] have been written describing detailed improvements in the process. It is not known how critical such controls are in the development of films having optimum mechanical properties at cryogenic temperatures.

For a laboratory study of this problem a small-scale simultaneous biaxial orientation apparatus was used.

2.3.2 Description of the "Hat Stretcher" Method of Biaxial Orientation

The basic unit for the biaxial orientation studies is shown in figure 2. This unit yields a film that has been simultaneously biaxially oriented.

Briefly, the unoriented sheet is clamped in a ring-shaped die, warmed by radiant heat, above the glass transition temperature of the polymer (its temperature measured by thermocouples pressed against its bottom surface), and then a hydraulic cylinder is raised up into the film to stretch it into the shape of a top hat.

Figure 3 shows the essential details of the ring clamp and the radiant heater, hinged back to take it out of the way. Figure 4 shows the heater hinged forward into position, warming the unoriented sheet by radiation. Figure 5 shows the heater hinged back again, the warm sheet ready to be stretched. The hydraulic cyclinder is next rapidly raised from beneath, stretching the sheet into the shape of a "top-hat" as shown in figure 6. The cylinder is then withdrawn again as shown in figure 7 and the stretched material is removed as seen in figure 8. The top surface has been uniformly biaxially oriented, as can be shown by examining it between crossed polarizers, or by printing a rectangular grid on the sheet before stretching and then examining the expanded grid on the film after stretching.

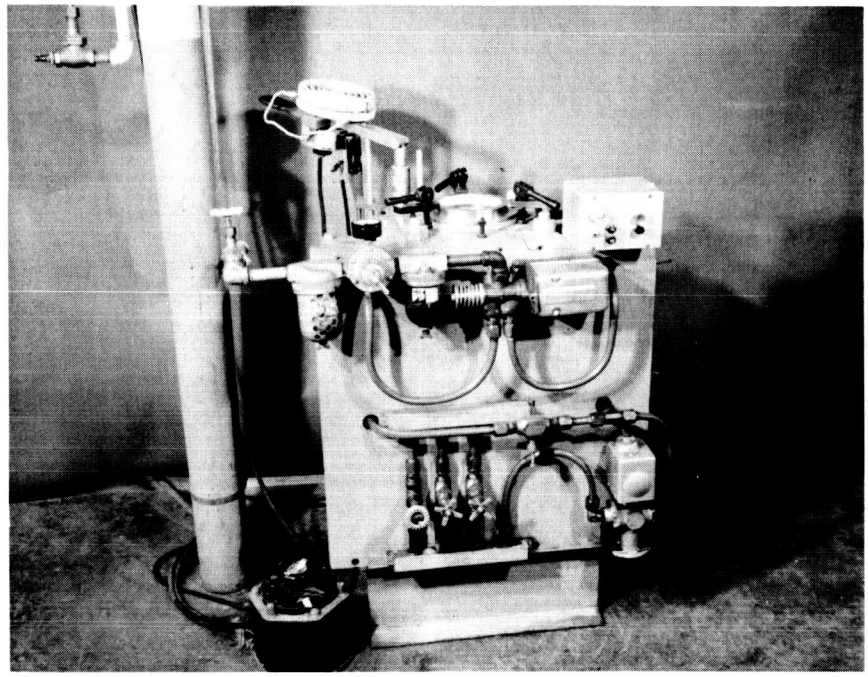


Figure 2. One-Stage Simultaneous Biaxial Orientation Unit at DeBell and Richardson -- "Hat Stretcher"

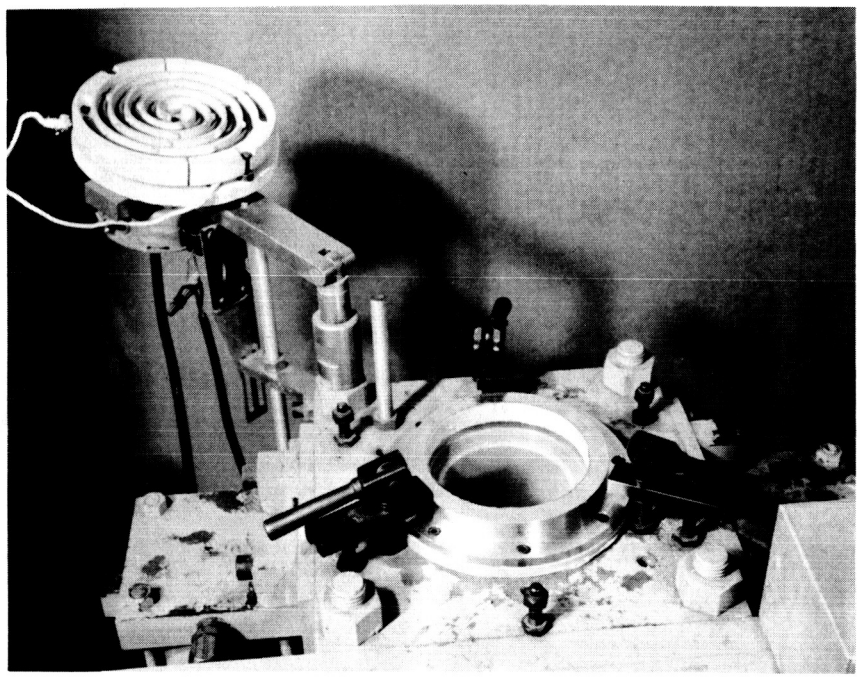


Figure 3. "Hat-Stretcher" -- Ring Clamp and Radiant Heater (Hinged Back)

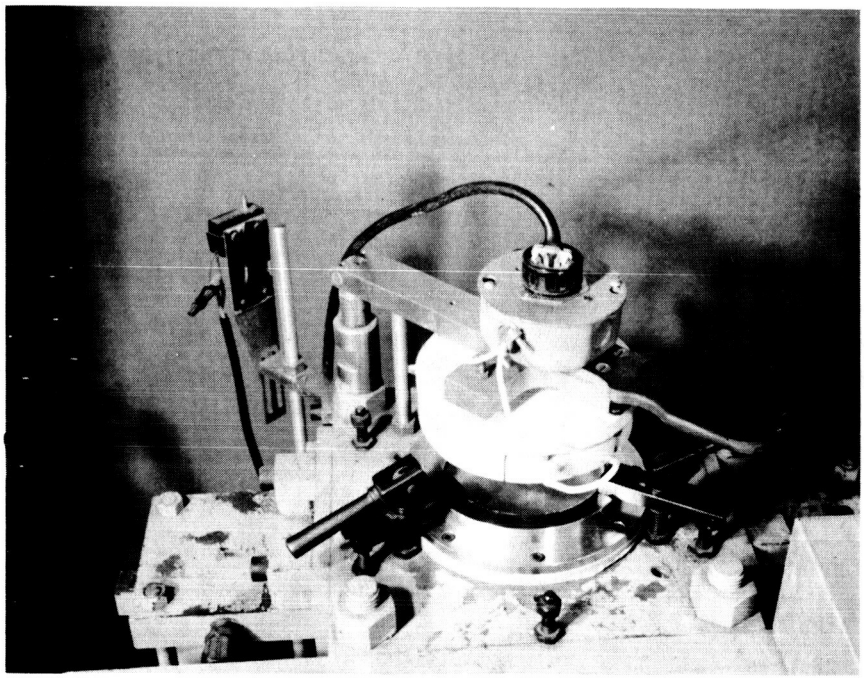


Figure 4. "Hat-Stretcher" -- Heater Hinged Forward Into Position to Heat Unoriented Sheet by Radiation

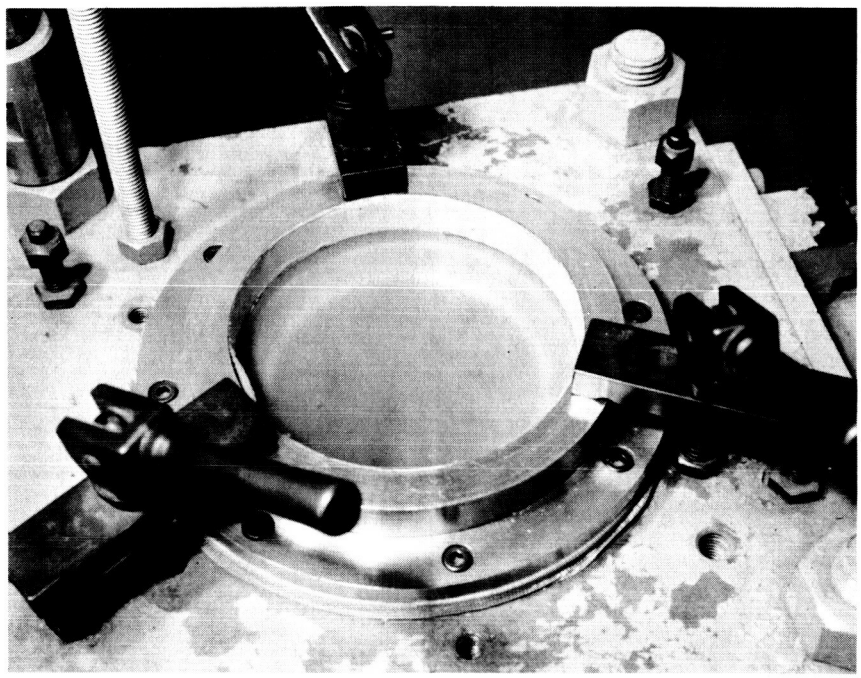


Figure 5. "Hat-Stretcher" -- Heater Hinged Back Again with Warm Sheet Ready to be Stretched

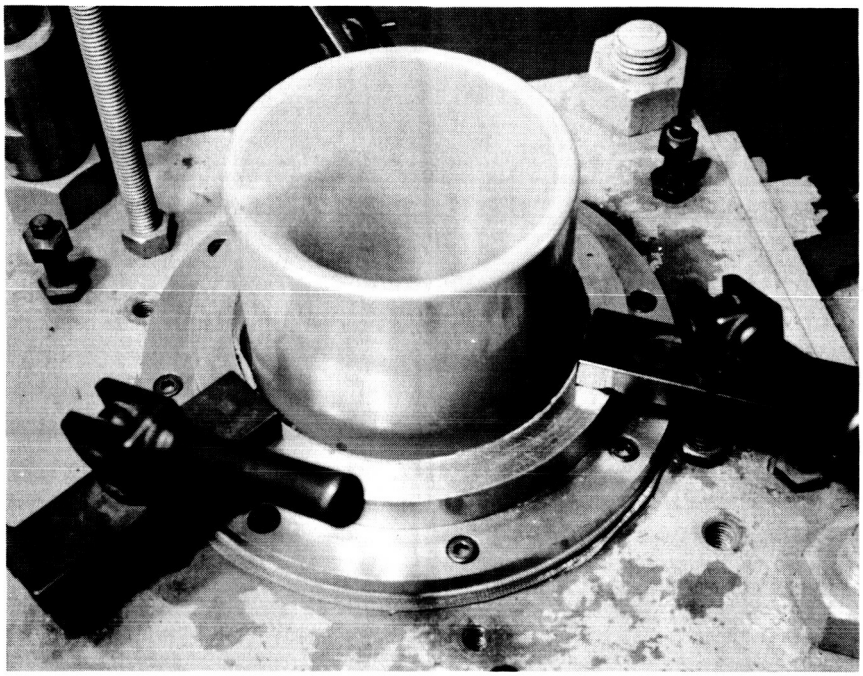


Figure 6. "Hat-Stretcher" -- Sheet Being Stretched by Hydraulic Cylinder Beneath It

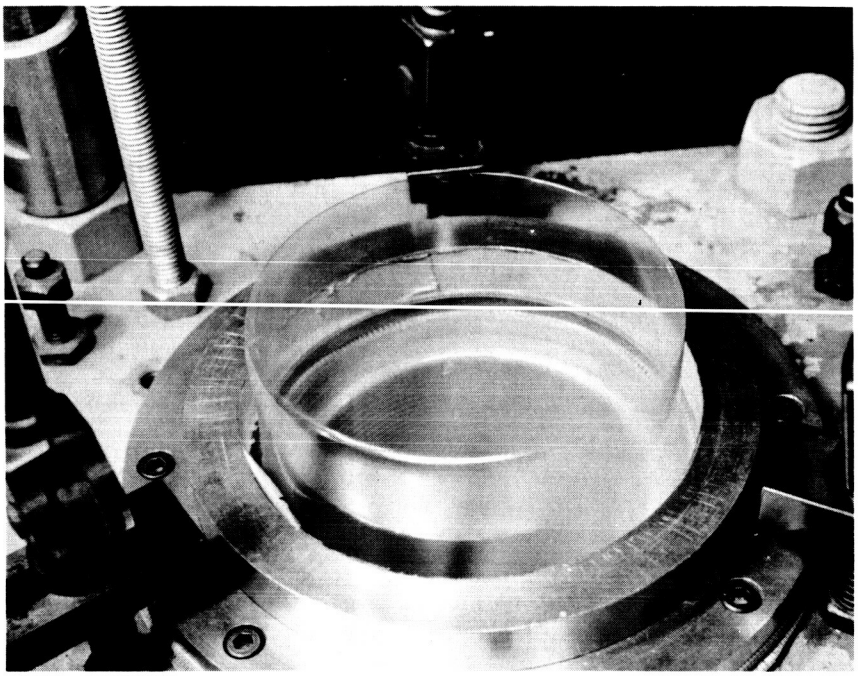


Figure 7. "Hat Stretcher" -- Stretched Sheet with Hydraulic Cylinder Being Withdrawn From It

2.3.3 Fabrication Studies on Poly(ethylene terephthalates)

a. Conversion of Film to Resin

Poly(ethylene terephthalate) is available commercially only in the form of oriented film. Since the manufacturers are unwilling to supply the virgin resin, a technique was developed for converting the film back into granular resin. When Mylar film Type A 0.014 in. thick was heated for 15 minutes at 260°C it crystallized into a brittle sheet which was readily ground into granular form. This change was due only to loss of orientation and increase of crystallinity; the granular resin retained its good color and melt index, indicating no degradation of molecular weight or structure.

Polymer	Melt Index at 290°C and 2160 Gm.
Virgin Mylar Tape A film	4.58-4.67 Gm.(per 10 minutes)
Heated 15 minutes at 260°C	4.09-4.67 Gm.(per 10 minutes)

On the other hand, more severe heat-aging for 20 minutes at 290°C produced a significant increase in melt index to 5.21, indicating some loss of molecular weight under those conditions.

b. Molding of Sheets

Commercial production of poly(ethylene terephthalate) film begins by extrusion of granulated resin into sheets at 270-315°C followed by quenching to 60-80°C to produce an amorphous film starting material for subsequent orientation. Since this process requires relatively large quantities of material, compression molding appeared more suitable for this program. When Mylar Type A resin was molded into 0.010 in. sheets between nickel or chrome platens at 275°C, and then quenched by cooling the mold, the sheets adhered tightly to the platens and could not be removed, even with the use of silicone and fluorocarbon mold release agents. Satisfactory release of the molded polymer was attained by coating aluminum mold platens with solid sheets of Teflon. Molded polymer sheets were quenched rapidly by cooling the mold directly in the press; instant quenching in cold water was also studied, but proved unnecessary, since press-cooling was more convenient and produced satisfactory densities of 1.33, indicating that no crystallization had occurred during cooling. When the resin was used as made, the moldings contained numerous bubbles. However, when the resin was vacuum-dried for 6 hours at 100°C, satisfactory bubble-free molded sheets were produced. It was also noted that the solid resin must be pre-heated in a barely-closed mold, to soften it before applying pressure, in order to avoid damage to the soft Teflon coating and consequent imperfections in the resulting molded sheets.

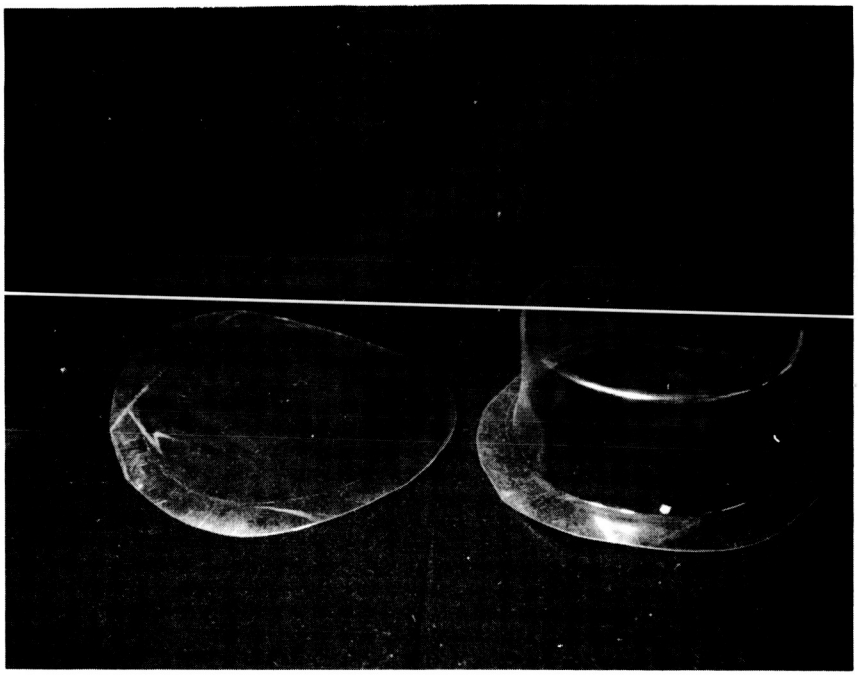


Figure 8. Stretched Sheet -- Biaxially Oriented

It was also found that amorphous sheet could be produced directly without going through the resin stage. This was done as follows: Commercial Mylar A 14-mil sheet was vacuum-oven-dried for 6 hours at 100°C and kept in a desiccator until used. The dried material was molded into unoriented amorphous 11-12 mil sheet between the Teflon-coated aluminum platens, by preheating 4.5 minutes at 0 (kiss) pressure, molding 0.5 minute at 275±2°C, and quenching for 2 minutes in a cold press before opening the mold. These sheets had specific gravities of 1.338-1.341, indicating very little crystallinity, and had an ultimate tensile strength of 5800 psi and elongation of 530%.

c. Simultaneous Biaxial Orientation

Unoriented amorphous 11-12 mil sheets were clamped in the D&R hat-stretcher and warmed by radiant heat for 11-18 seconds. Thermocouples fastened to the bottom of the sheet indicated that temperatures of 79-101°C were attained according to the heating time. Thermocouples at the center of the sheet averaged 2-3°C higher than at the edge of the sheet, because the center of the sheet was the recipient of more angular radiation than the edges were.

Stretching was accomplished by raising the hydraulic cylinder at a rate which stretched the film 14,400-36,000 percent/minute, drawing 11-12 mil sheet down to 0.2-2.5 mil film. Stretch ratios of 2.2 x 2.2 up to 7.1 x 7.1 were attained as calculated by computing the square root of the ratio of the original to the final film thickness.

Densities were measured in carbon tetrachloride/hexane solutions. It was observed that stretching a film 2.2-5.5X increased its density to 1.355-1.359, while stretching a film 7.1 X.7.1 increased its density to 1.359-1.363, thus indicating development of low crystallinity during stretching.

Uniformity of thickness of stretched films varied from sample to sample. For example, one sample had a total range of thicknesses from 0.7 to 0.9 mils, whereas another ranged from 1.0 to 4.9 mils. When there was a wide range of thicknesses in the final sample, their pattern indicated random asymetric effects such as room air currents or similar factors, which indicated the need for more precise control of film temperature.

Uniformity of heating on the hat-stretcher was improved by mounting a 3-in. diameter 20-mesh galvanized screen 3/4 in. below the heating element and 1.5 in. above the film sample; this permitted production of uniformly stretched samples. Molded sheets 13 mils thick were heated to 91 and 101°C and stretched 4X down to 0.75 mil and specific gravity 1.35, then clamped on frames and heat-set 0, 10, and 30 seconds at 200°C to specific gravity 1.39. Molded sheets 18 mils thick were heated to 112°C and stretched 6X down to 0.5 mil, then clamped on frames and heat-set

10 seconds at 200°C to specific gravity 1.42. These films were tested for twist-flex life, tensile properties, permeability, and coefficient of thermal expansion. Listed below are the conditions used in preparing the five sets of films which were tested:

Temperature of Drawing(°C)	Draw Ratio Applied	Heat-Setting Time at 200°C	Final Thickness	Final Density
91	4 X 4	10 Seconds	0.8 Mils	1.36
101	4 X 4	0 "	0.75 "	1.36
101	4 X 4	10 "	0.85 "	1.39
101	4 X 4	30 "	0.8 "	1.39
112	6 X 6	10 "	0.5 "	1.42

d. Sequential Biaxial Orientation

The Tennessee-Eastman Co. supplied NASA Lewis for use in this program, a series of sequentially biaxially oriented Eastman PET film samples which were produced on a "T.M. Long" laboratory biaxial orientation apparatus. Non-uniformity in thickness of film samples were noted in some cases reducing their value for twist-flex testing. Film samples which were usable were heat-set 10 seconds at 200°C, and are described in the tabulation on page 38; where sufficient material was available, a second portion was left stretched-but-not-heat-set for comparison. Several of these films were tested for twist-flex life, tensile properties, permeability and coefficient of thermal expansion and showed promising results for one set of orientation conditions.

e. Large Scale Sequential Stretching of PET Amorphous Sheet

An attempt was made to prepare larger sized film specimens of PET by utilizing the equipment available in the Customer Service Laboratory of the Marshall and Williams Co. of Providence, R.I.

This equipment requires the use of 12 inch wide unoriented amorphous sheet. This sheet is fed to a longitudinal stretcher which warms the sheet on a slow speed oil-heated roll, then stretches it onto a faster speed oil-heated roll, and then quenches it back to room temperature. This reduces the transverse width somewhat. The longitudinally-stretched roll, at least 8 in. wide, is then fed through a pair of chains of tenter frame clamps in a multi-stage air oven, which first heats the sheet, then stretches it transversely according to any desired pre-set pattern, and finally heat-sets it before winding it up again. In order to carry out this operation a 12 inch diameter roll of 12 inch wide sheet wound on a 3 inch core is generally required.

For this purpose, duPont supplied NASA-Lewis with short rolls of 30 inch wide 10, 15, 25, and 35-mil unoriented amorphous Mylar A sheet, wound on 6 inch cores. These were each slit into two 12 inch and one

CONDITIONS FOR PRODUCTION OF SEQUENTIALLY STRETCHED FILMS FROM TENNESSEE-EASTMAN

Sample	Stretch Temp. °F	Stretch	Rate of Stretch, In./Min.	Thickness of Film		Density of Film		Usable 4" x 4" Samples	
				As Rec'd. Mils	Heat-Set Mils	As Rec'd	Heat-Set	Heat-Set	Not Heat-Set
B	168-176	2.0	0.5	0.3-0.7	0.3-0.5	1.350	1.382	3	--
B-1	168-176	2.0	8.0	0.3-0.8	0.5	1.363	1.382	3	--
E	168-172	3.5	0.5	0.2-0.7	0.5		1.393	6	6
E-1	168-172	3.5	8.0	0.3-0.8	0.5-0.7	1.362	1.397	6	6
F	170-175	4.0	0.5	0.5-1.0	0.5-1.0	1.353	1.387	6	6
G-1	198-204	4.0	8.0	0.4-0.8	0.5-0.9	1.371	1.394	6	6
I	200-208	2.0	0.5	0.2-0.5	0.1-0.4		1.364	3	--
I-I	200-208	2.0	8.0	0.2-0.6	0.2-0.4	1.366	1.388	3	--
K-1	200	3.0	8.0	0.6-1.0	0.5-0.7	1.367	1.392	6	6
L-1	200	3.5	8.0	0.5-0.8	0.4-0.7	1.364	1.395	6	6

8 inch width, rewound on 3 inch cores, and taken to Marshall and Williams for stretching. The lengths proved too short, and M&W was unable to find optimum stretching conditions before they ran out of material. They finally produced some small samples by stretching 10-mil sheet 3X at 66°C by 3X at 143°C, 15-mil sheet 4X at 66°C by 2-3.4X at 132-143°C, and 35-mil sheet 5X at 96°C by 4X at 99°C; but these were too thick for useful twist-flex testing.

In order to prepare larger quantities of amorphous sheet for additional stretching studies at M&W, extrusion studies were undertaken as follows: Mylar A 14-mil sheet was chopped in a Cumberland Engineering Model 1420 granulator to pass a 3/16 inch diameter screen, dried 3 hours at 93°C in a circulating air oven, extruded through a 1.5 inch MPM Co. extruder with a "nylon" type screw in an optimum temperature range of 266-282°C to balance complete melting against minimal degradation, and cast onto a 55-80°C chill roll to produce 10 inch wide unoriented uncrystallized sheet 3-12 mils thick. This sheet was quite satisfactory for hat-stretching, but was not satisfactory for stretching at M&W since "gel spots" and "fish-eyes" were present in various places through the rolls so prepared. Large scale extrusion studies were discontinued by direction of the NASA-Lewis Project Manager in order to concentrate efforts on fabrication studies of synthesized polymers, since defect-free material production did not appear possible without extensive work.

2.3.4 Fabrication Studies on Poly(ethylene isophthalate)

Poly(ethylene isophthalate) was molded at 204-210°C to form 10-mil sheets which contained some gel particles. These sheets were oriented on the hat stretcher at 100°C and 4X stretch and handled fairly well but would require further study to produce uniform films large enough for twist-flex testing. Small film specimens of fairly uniform material were produced for tests other than twist-flex, and these results are reported in the appropriate sections below.

Solvent casting of poly(ethylene isophthalate) from 10% chloroform solutions on glass plates produced 0.7-1.5 mil films after drying overnight at room temperature. These films were quite soft and tended to wrinkle during drying and handling. Again, only enough material was produced for tests other than twist-flex.

2.3.5 Fabrication Studies on Other Polymers

a. Poly(diethyleneoxy terephthalates).

Poly(diethyleneoxy terephthalate) resin was soft and tacky at room temperature. It could be cold-pressed to form films, but these tended to adhere to the platens and exhibited rubbery retraction when removed. Solution-casting, of 10% solutions in chloroform, produced 7-mil wet films on glass plates, which dried overnight at room temperature to 0.7-mil dry films; these were too soft, sticky, and weak to be removed from the glass plates. Mylar, silicone, and Teflon release agents all caused discontinuous castings which did not form films at all.

b. Poly(trimethylene terephthalates)

Poly(trimethylene terephthalate) was molded at 238°C to form 8-mil sheets which were fairly clear but very brittle. When heated and oriented on the hat-stretcher at several temperatures (above Tg) the films became opaque rapidly, and broke during processing. The major difficulty was probably extremely rapid crystallization. This polymer has been reported in the literature to undergo rapid crystallization even when quenched rapidly from the melt.[11]

c. Poly(tetramethylene terephthalates)

Poly(tetramethylene terephthalate) was molded at 246°C to form 8-mil sheets; but these were opaque and extremely brittle, and impossible to stretch or even handle without crumbling. The major difficulty was probably extremely rapid and excessive crystallization. This polymer has also been reported to undergo rapid crystallization even when quenched rapidly from the melt.[11]

d. Poly(2,6-dimethylphenylene oxide)

Poly(2,6-dimethylphenylene oxide) PPO resin was molded at 277-316°C to form 1-10 mil films and sheets, but these were poorly fused, rough-surfaced, and shrank on cooling. Solution-casting, of 10% solutions in chloroform, produced 7-mil wet films on glass plates, which dried overnight at room temperature to 0.7-1.5 mil films of fairly good quality, which were satisfactory for testing.

e. Celcon

Celcon formaldehyde copolymer from Celanese Plastics Co. was difficult to mold at 177-204°C to form satisfactory uniform sheets for hat-stretching. Semicommercial 15-mil sheet from Celanese was more uniform and could be oriented on the hat-stretcher at 160-177°C and 4X stretch; but temperature requirements for this polymer were too critical, and the films always broke during the stretching operation.

2.4 Twist-Flex Testing

2.4.1 Twist-Flex Test Method Studies

During the early part of the twist-flex testing program several discrepancies quickly became apparent. For one, Melpar's twist-flex apparatus appeared to yield twist-flex endurance cycle values equal to approximately one-half those obtained by NASA-Lewis on their apparatus on comparable film materials. Another discrepancy arose during the testing of Mylar T film. Melpar obtained twist-flex data on Mylar type T which indicated that it was superior to Mylar C at liquid nitrogen temperature. Prior to this result NASA had concluded that Mylar T was inferior to Mylar C at this temperature. Accordingly the results obtained on Mylar T were considered questionable.

The following steps were taken to resolve these discrepancies: (1) determine the utility and limitations of the twist-flex method as a major overall objective and (2) define the various factors responsible for the reported discrepancies.

As an initial step, it appeared desirable to determine, (1) whether there was any difference in the operational techniques in handling of the films and use of the twist-flex equipment, and (2) whether there was any difference in the performance of the twist-flex machines at Melpar and at NASA. To resolve this question, Mr. E. Sanford of Melpar went to NASA-Lewis to perform the same tests using the NASA twist-flex apparatus.

Mr. Sanford found that (1) his handling of the films was no different than that of the NASA technician, and (2) that there was no difference in the performance of the twist-flex machines at Melpar and at NASA-Lewis. The natural scatter in the data caused Melpar to select a lower failure level than NASA, though this is certainly a matter of interpretation. Figure 9 shows some data on multiple specimens of Mylar T compiled at Melpar and NASA and it is apparent that the respective twist-flex machines yielded, for all practical purposes, identical results.

In regard to the relative performance of Mylar T at Melpar and NASA-Lewis, it was found that the original results at NASA on Mylar T were obtained on samples that did not have their ends reinforced by tape or heat sealing. Rerunning samples of Mylar T at NASA-Lewis with reinforced ends confirmed the Melpar observation that Mylar T is superior to Mylar C in twist-flex endurance at liquid nitrogen temperature.

A pertinent fact relevant to defining a characteristic cycles to failure value for Mylar T by the twist-flex method was the unexpected failure of certain Mylar T film speciments of the 4 in. x 11 in. size at a very low number of cycles. As can be seen in figure 9, a certain proportion of the films failed at various cycle levels.

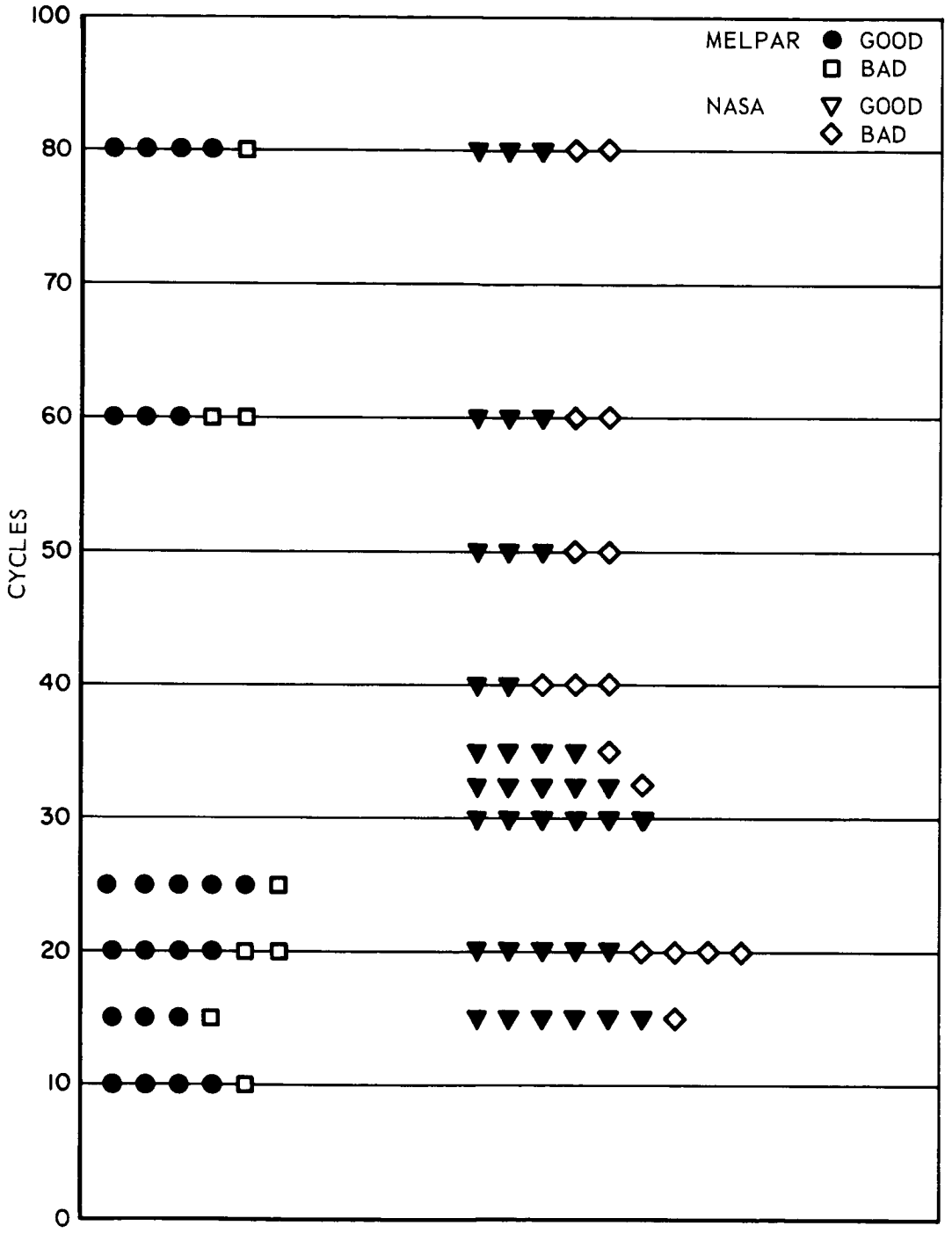


Figure 9. Twist-Flex Data -- Mylar T, 1/2-Mil, LN_2 Temperature, 4 in. x 11 in., MD↓

Based on this information it appeared that the problem resided at least in part in the presence of defects or "weak spots" in Mylar T and that these were the sites where most of the observed failures at a very low number of cycles occurred. In those cases where high twist-flex endurance was observed the possibility exists that those particular films were essentially defect-free.

To determine whether there were certain "defect areas" in the original roll of Mylar T film, a collaborative test program with NASA-Lewis was carried out. This test program also presented an opportunity for another comparison between results from Melpar's and NASA-Lewis twist-flex test procedures.

Two lineal yards of 1/2 mil Mylar Type-T were cut into 4 x 11-inch test sections. Melpar tested half of these at liquid nitrogen temperature, and NASA tested the other half at the same temperature. All specimens were subjected to 25 cycles and tested for failure. Figure 10 shows these results and is apparent that the machines produced the same results. Further, the distribution of the failures showed no pattern with respect to location in the Mylar sheet.

Melpar also continued the study of 4 x 4-inch Mylar-Type-T specimens (1/2-mil) at liquid nitrogen temperature. Samples of the film were found to withstand over 350 cycles without failing. This again demonstrated the superiority of Mylar Type-T to the other films that had been tested, since Mylar C, of this sample size, failed after about 75 cycles at liquid nitrogen temperature. It appears therefore that the failure of some 4 in. x 11 in. Mylar T samples at relatively low cycle values is characteristic of the sample size since the 4 in. x 4 in. sized samples showed only a very small number of early failures over the range of 350 cycles.

The results of twist-flex testing of other types of poly (ethylene terephthalate) films of the 4 in. x 11 in. size as compared to the 4 in. x 4 in. size indicate that early failures also occur in the 4 in. x 11 in. size samples of these materials (See 2.4.2 below). The purpose in studying smaller sized film specimens was to establish base-line values for commercial films since in all cases only limited amounts of experimental films were available.

In response to a request by the NASA-Lewis Project Manager, a series of tests were run to determine whether or not there were any differences in twist flex results as a consequence of the position of the sample on the twist-flex fixture. To accomplish this, two 4 x 4 inch speciments of Mylar (1-mil) Type C were run simultaneously at room temperature, one clamped on the front and one clamped on the back of the fixture. The samples were subjected to 130 cycles, which is slightly more than the average lifetime determined by previous tests on this apparatus (see figure 17). Ten such

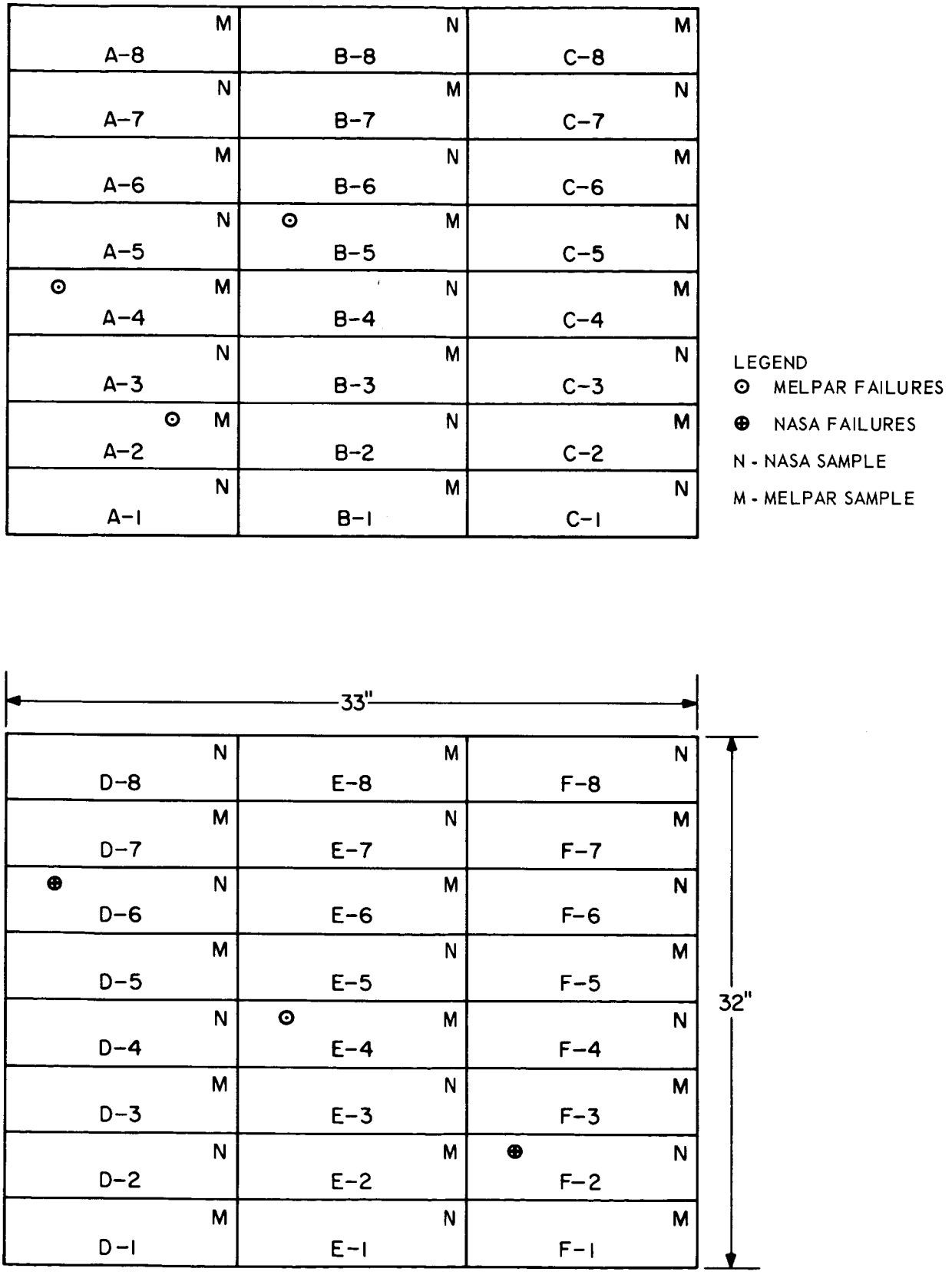


Figure 10. Distribution of Specimens of 1/2 Mil Mylar T For Twist-Flex Testing

tests were conducted and there was no significant difference noted for any of the samples. Failure was random and occurred on both the front and back specimens almost equally distributed.

2.4.2 Twist-Flex Endurance As A Function of Film Specimen Size

a. Mylar C

In order to be able to twist-flex experimental samples of films of smaller size, calibration experiments were carried out on Mylar C. These tests were carried out on three different sized samples, namely 4 x 11 inch, 4 x 4 inch and 4 x 2-3/4 inches. Both 1-mil and 1/2-mil Mylar C were tested in the two larger sizes at room temperature and at liquid nitrogen temperature. The 1/2-mil Mylar C was tested in the smallest size (4 x 2-3/4) at liquid nitrogen temperature only.

In the measurements at liquid nitrogen temperature, it was necessary to reinforce the edge of the specimen to prevent failure due to splits from end effects. Although the NASA-Lewis Project Manager suggested the use of tape to provide the necessary reinforcement; a satisfactory substitute was to fold over 1/16 inch at each end of the 4- by 4-inch specimen and to seal them with an impulse sealer. In all cases, the sample holder was cooled to liquid nitrogen temperature before loading samples to help minimize any defects due to thermal contraction.

As can be seen in the following figures, 11 through 19, the size and thickness of the specimen has a profound effect on the twist-flex endurance of Mylar C and no doubt this effect would manifest itself in any film subjected to this type of comparison.

The relative results for the 1/2-mil Mylar C film at liquid nitrogen temperature were as follows: 4 x 11 inch sample, approximately 35 cycles; 4 x 4 inch sample, approximately 75 cycles; and the 4 x 2-3/4 inch sample, approximately 700 cycles.

b. Mylar T

Another set of comparison experiments was carried out in a similar fashion on Mylar T, 1/2-mil, at liquid nitrogen temperature. The 4 x 11 size specimens yielded a wide scatter of results discussed in section 2.4.1 and shown in figure 9 above. Another size of Mylar T namely 4 in. x 7-1/2 in. was tested and as shown in figure 20 yielded only one failure up to 220 cycles out of eleven specimen tested. The 4 in. x 4 in. sized specimens were tested in both longitudinal and transverse directions. In the longitudinal direction 10 specimens were tested up to 450 cycles without failures. Two additional specimens at 475 cycles and at 500 cycles showed failure. These data are shown in figure 21. A large number (54) of tests were carried

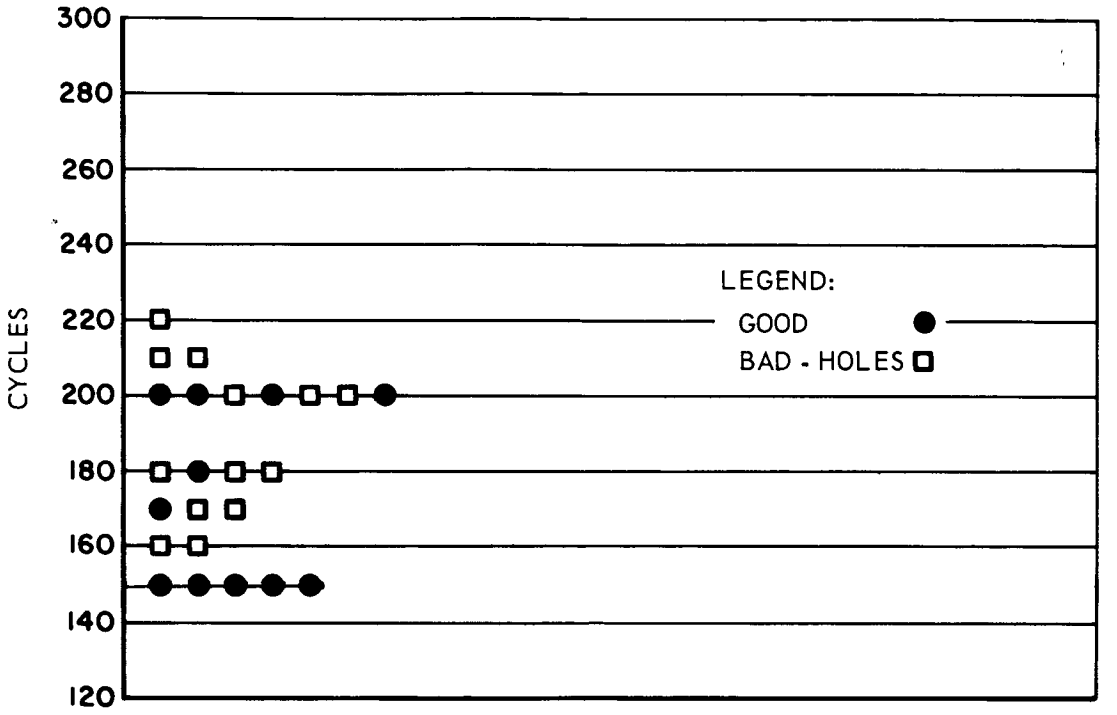


Figure 11. Twist-Flex Data -- Mylar C, 1/2-Mil, Room Temperature 4 in. x 11 in., MD.

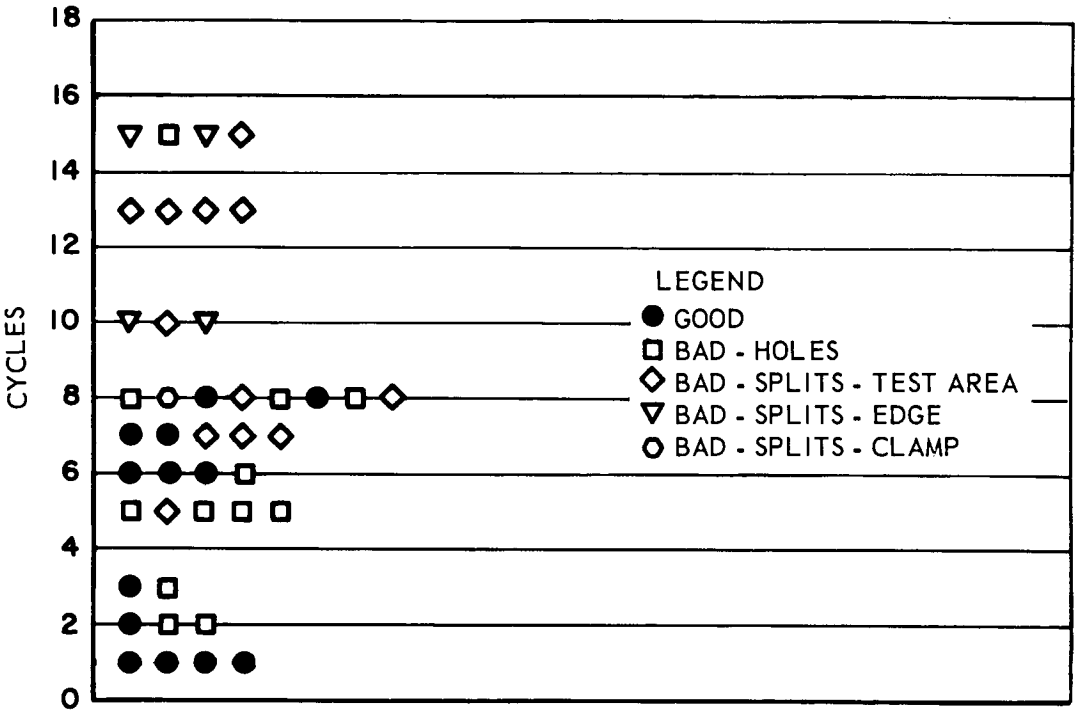


Figure 12. Twist-Flex Data -- Mylar C, 1-Mil LN_2 Temperature, 4 in. x 11 in., MD

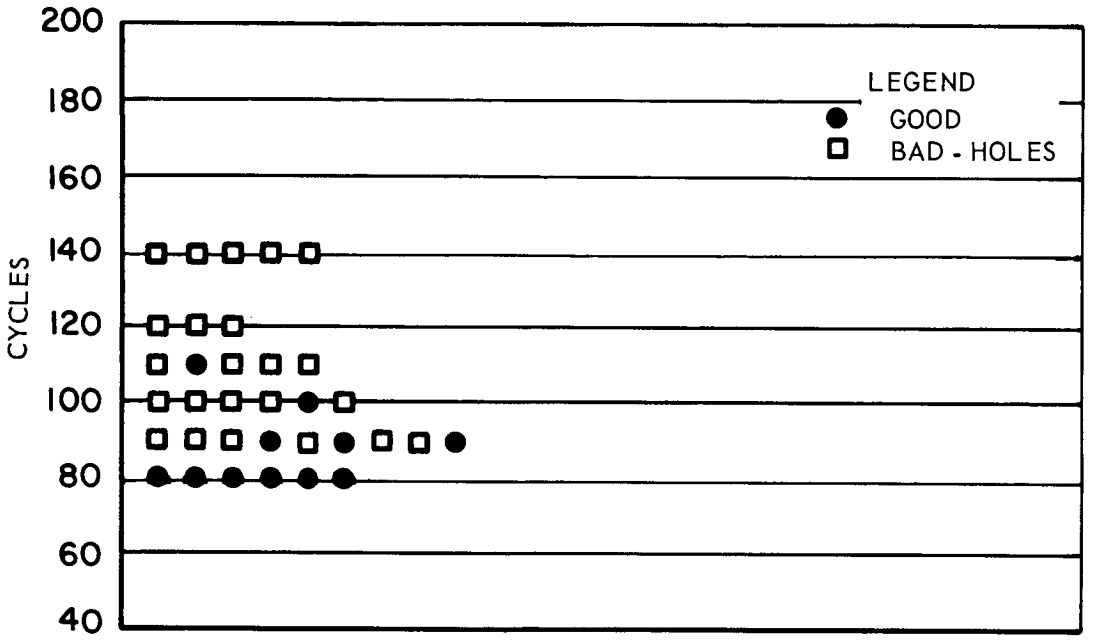


Figure 13. Twist-Flex Data -- Mylar C, 1-Mil Room Temperature, 4 in. x 11 in., MD→.

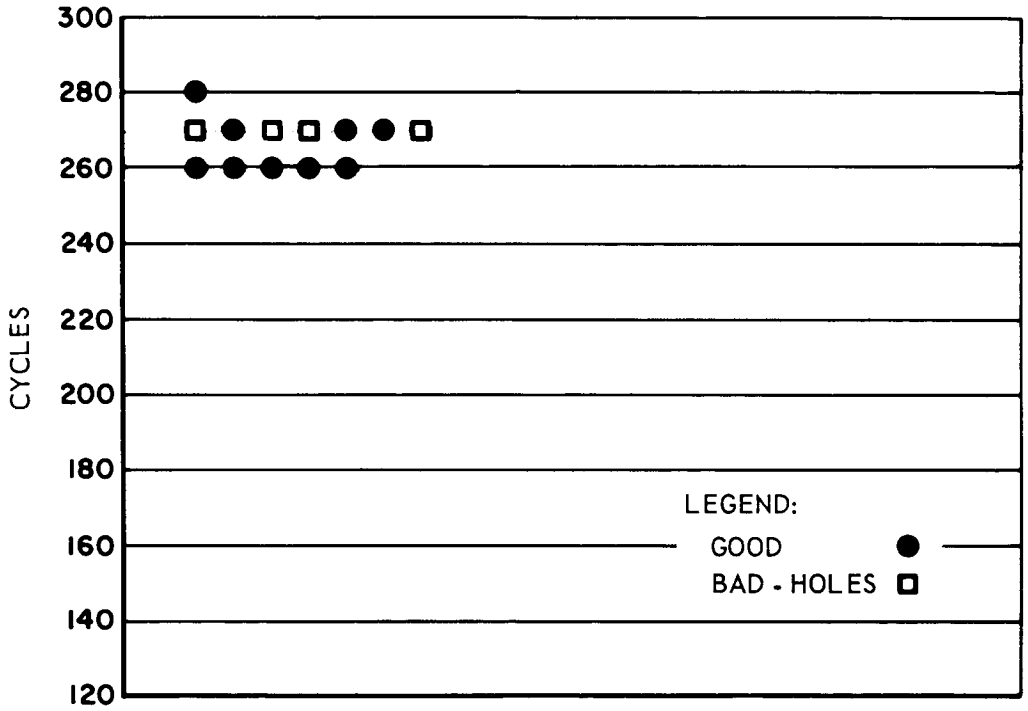


Figure 14. Twist-Flex Data -- Mylar C, 1/2-Mil Room Temperature, 4 in. x 4 in., MD→.

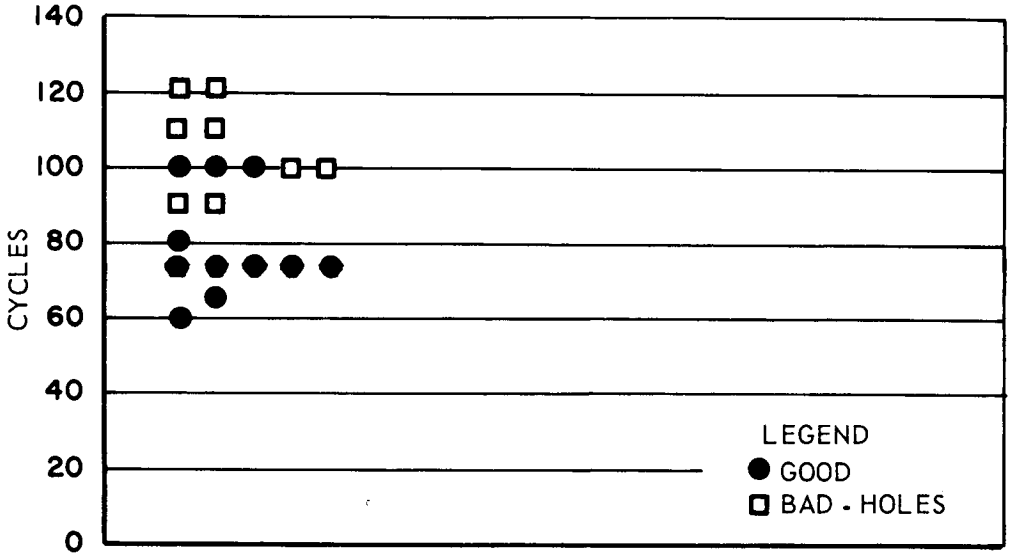


Figure 15. Twist-Flex Data -- Mylar C, 1/2-Mil LN_2 Temperature, 4 in. x 4 in., MD→.

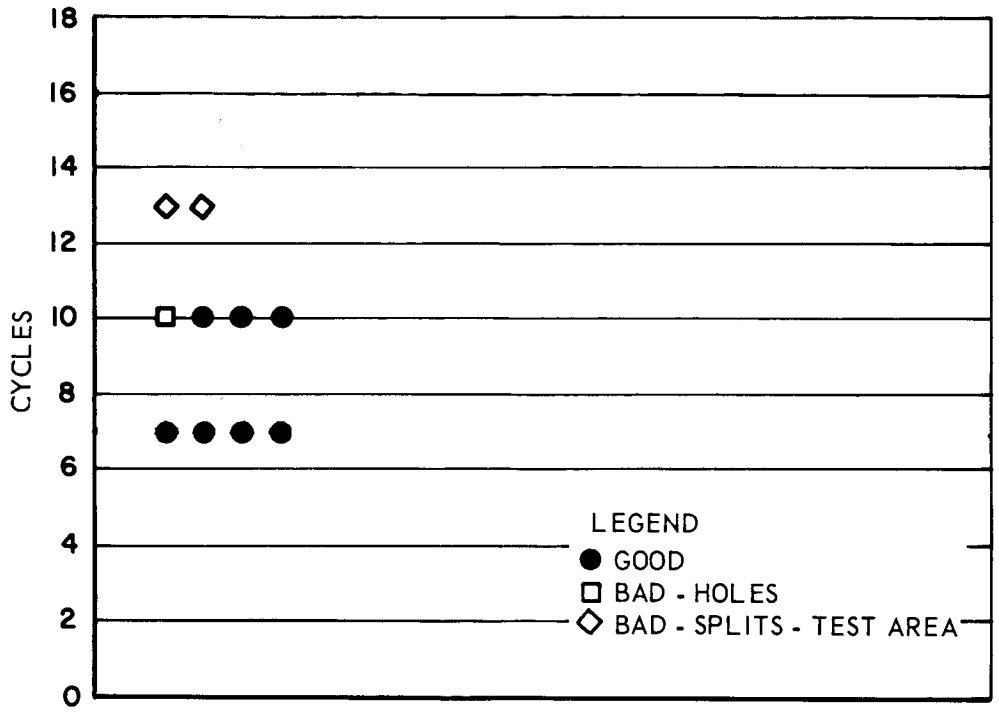


Figure 16. Twist-Flex Data -- Mylar C, 1-Mil LN_2 Temperature, 4 in. x 4 in., MD→.

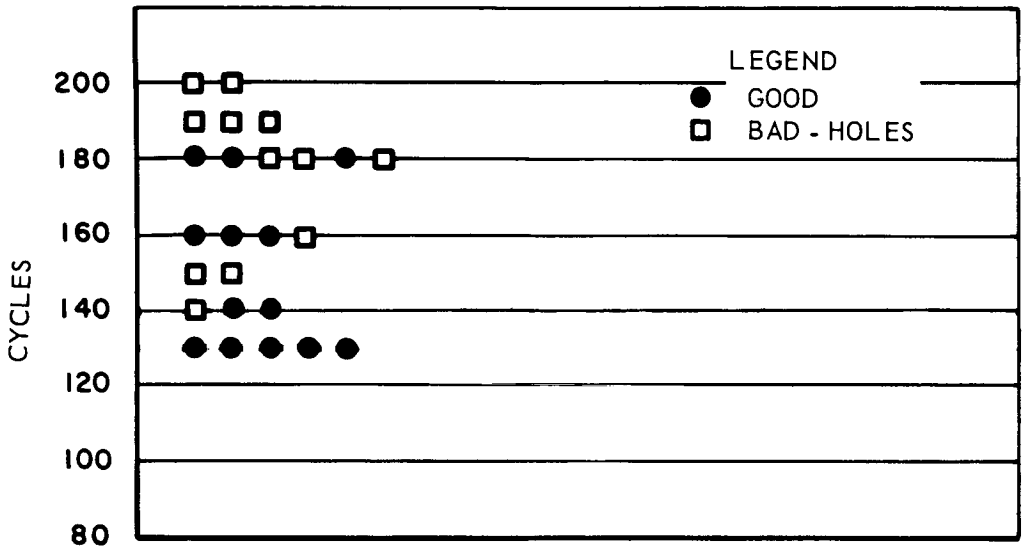


Figure 17. Twist-Flex Data -- Mylar C, 1-Mil Room Temperature, 4 in. x 4 in., MD→

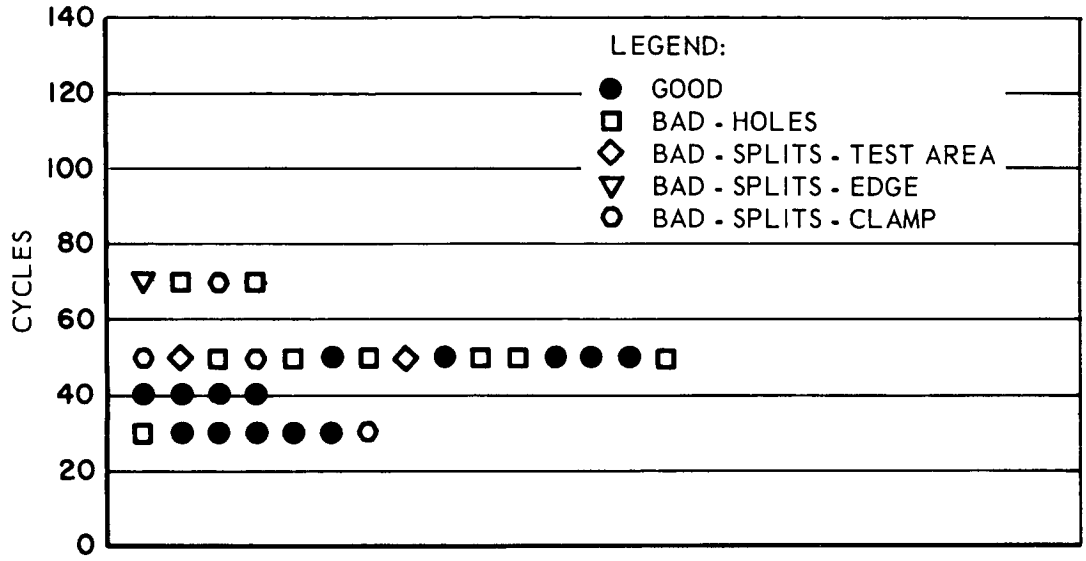


Figure 18. Twist-Flex Data -- Mylar C, 1/2-Mil LN_2 Temperature, 4 in. x 11 in., MD→.

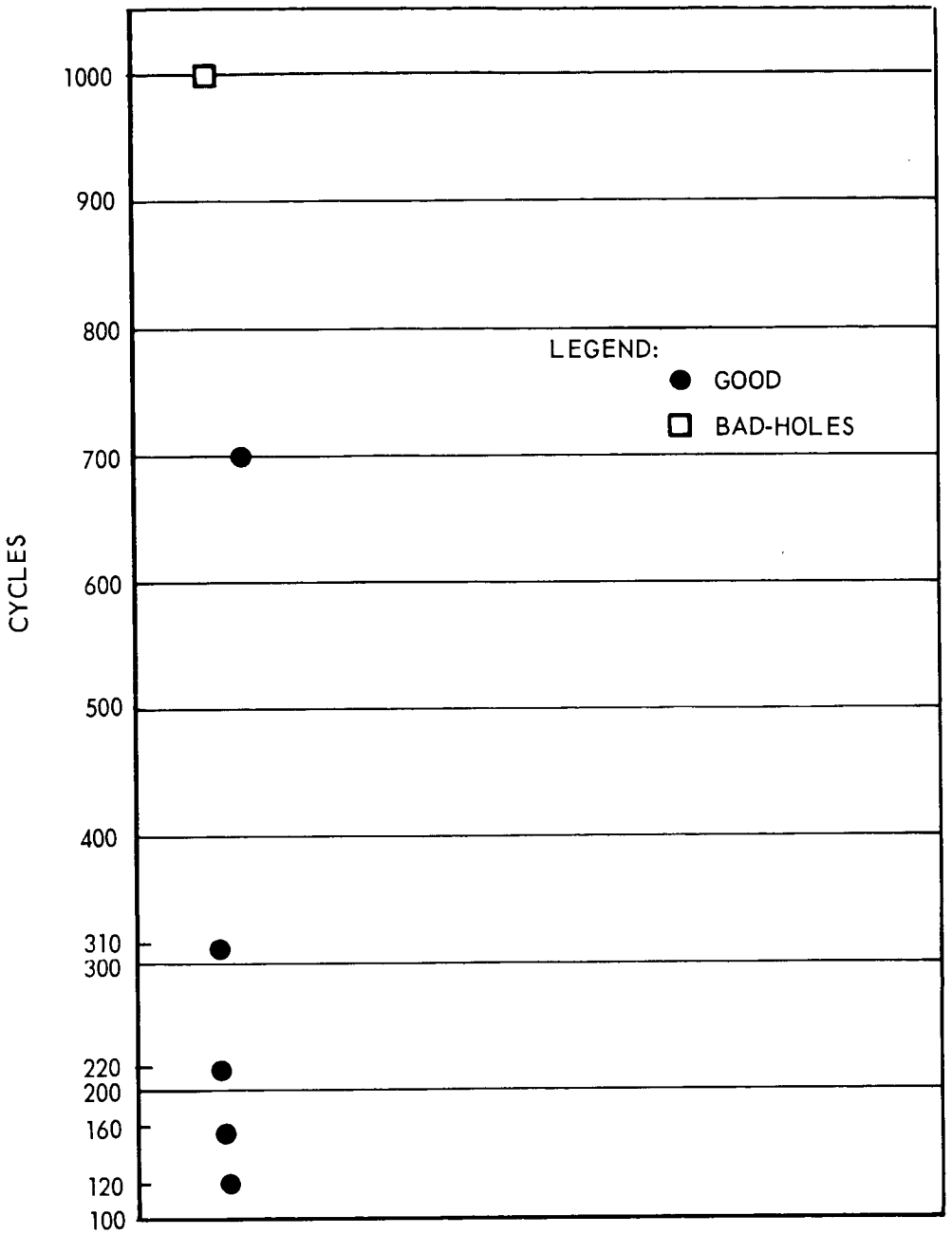


Figure 19. Twist-Flex Data-- Mylar C, 1/2-Mil LN_2 Temperature, 4 in. x 2-3/4 in.

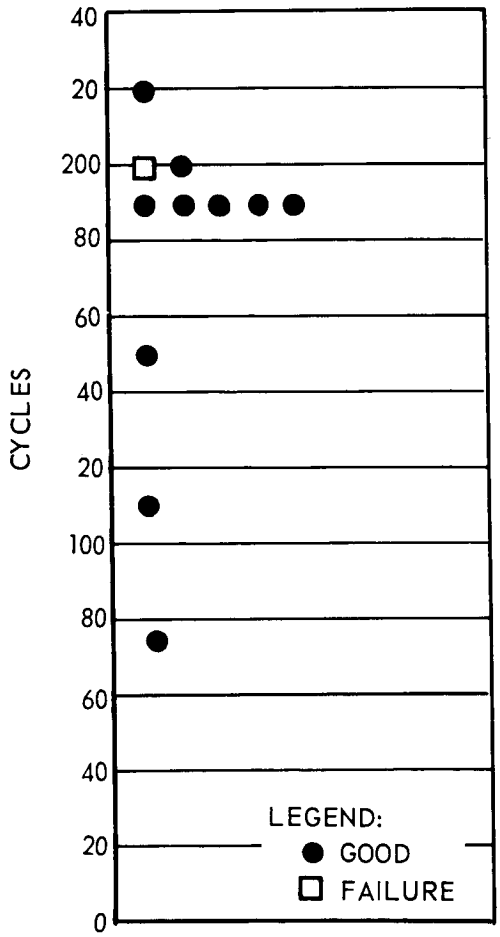


Figure 20. Twist-Flex Data -- Mylar T, 1/2-Mil LN_2 Temperature, 4 in. x 7-1/2 in., MD↓.

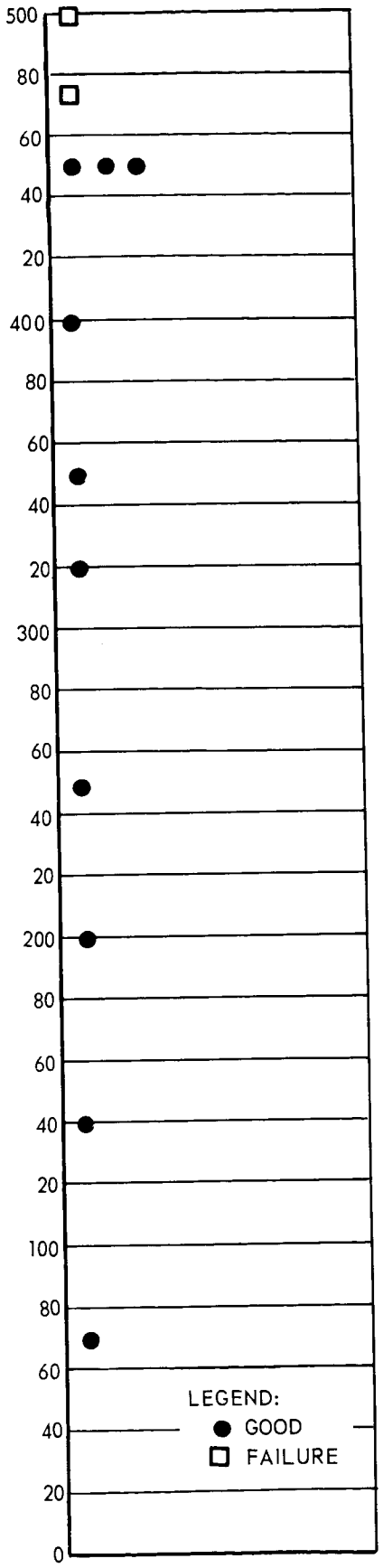


Figure 21. Twist-Flex Data -- Mylar T, 1/2-Mil LN_2 Temperature, 4 in. x 4 in., MD→.

out on specimens in the transverse direction. These tests showed only three early failures and indicate that twist-flex life here is on the order of 400 cycles as shown in figure 22. For the 4 in. x 2-3/4 in. size film specimen no failures were observed up to 2000 cycles. (See figure 23.)

2.4.3 Twist-Flex Data for Various Commercial Films

Twist-flex testing was carried out on Mylar types A, C. and T Vitel VMF-414, Vitel VFR-338, Lexan, Kapton (H-Film) and Kodar. Kodar, Lexan and Kapton exhibited relatively poor twist-flex life. The limited amount of data obtained for Lexan and Kapton is shown in figures 24 through 27.

Kodar film is Tennessee Eastman's polyester film and is a modified poly (dimethylene cyclohexylene terephthalate). The exact nature of the modification is not known but probably involves either addition of plasticizer or copolymer. This modification serves to reduce the melting point from about 300°C down to about 275°C and aids in the processability of this material. The unmodified material is designated Type 0, while the modified material (used in making Kodar) is called Type 2.

The twist-flex resistance of Kodar was found to be less than that of Mylar C at room temperature and at liquid nitrogen temperature, and these tests were terminated prior to determining the exact number of cycles to failure.

The Vitel VMF-414 and Vitel VFR-338 films were obtained from the Goodyear Tire and Rubber Co. and are reportedly a copolymer of poly(ethylene terephthalate) and poly (ethylene isophthlate). Since these were obtainable only as 2-mil films a calibration for 2-mil film was made with 2-mil Mylar A (Mylar C is not produced in 2-mil size). Data for Mylar T is shown in figures 28, 29 and 30.

The data from these tests are shown in figures 31 and 36. From these data it can be seen that the two Goodyear films are approximately equal to Mylar A in twist-flex endurance.

2.4.4 Twist-Flex Data for Various Experimental Films

a. Twist-Flex Testing of Sequentially Biaxially Oriented PET Films Prepared by Tennessee Eastman.

Figure 37 shows the twist-flex data obtained for the above indicated films. The following observations can be made concerning the twist-flex life of PET films as a function of orientation parameters: (1) Heat-setting of PET films, after biaxial orientation, by heating at 200°C for 10 seconds had little or no effect on twist-flex life (for example, see results on specimens L-1, E-1, F and E, heat set and not heat set, in figure 37);

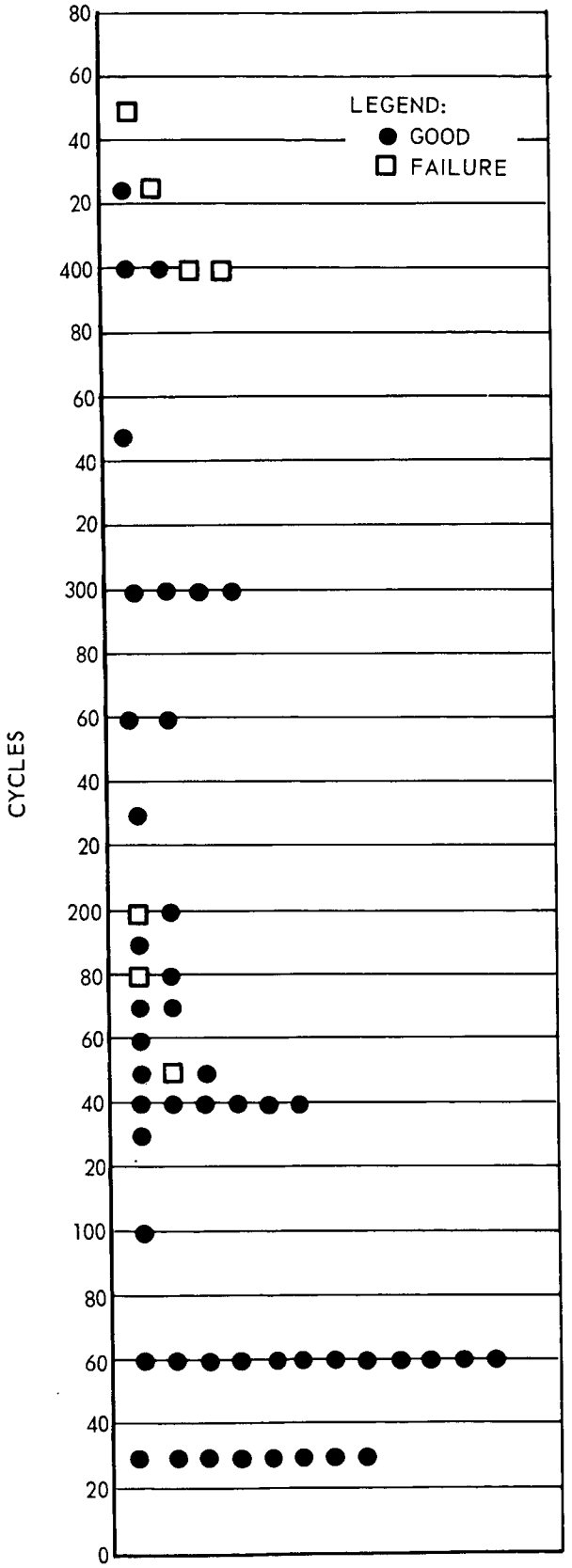


Figure 22. Twist-Flex Data -- Mylar T, 1/2-Mil LN_2 Temperature, 4 in. x 4 in., MD ↓.

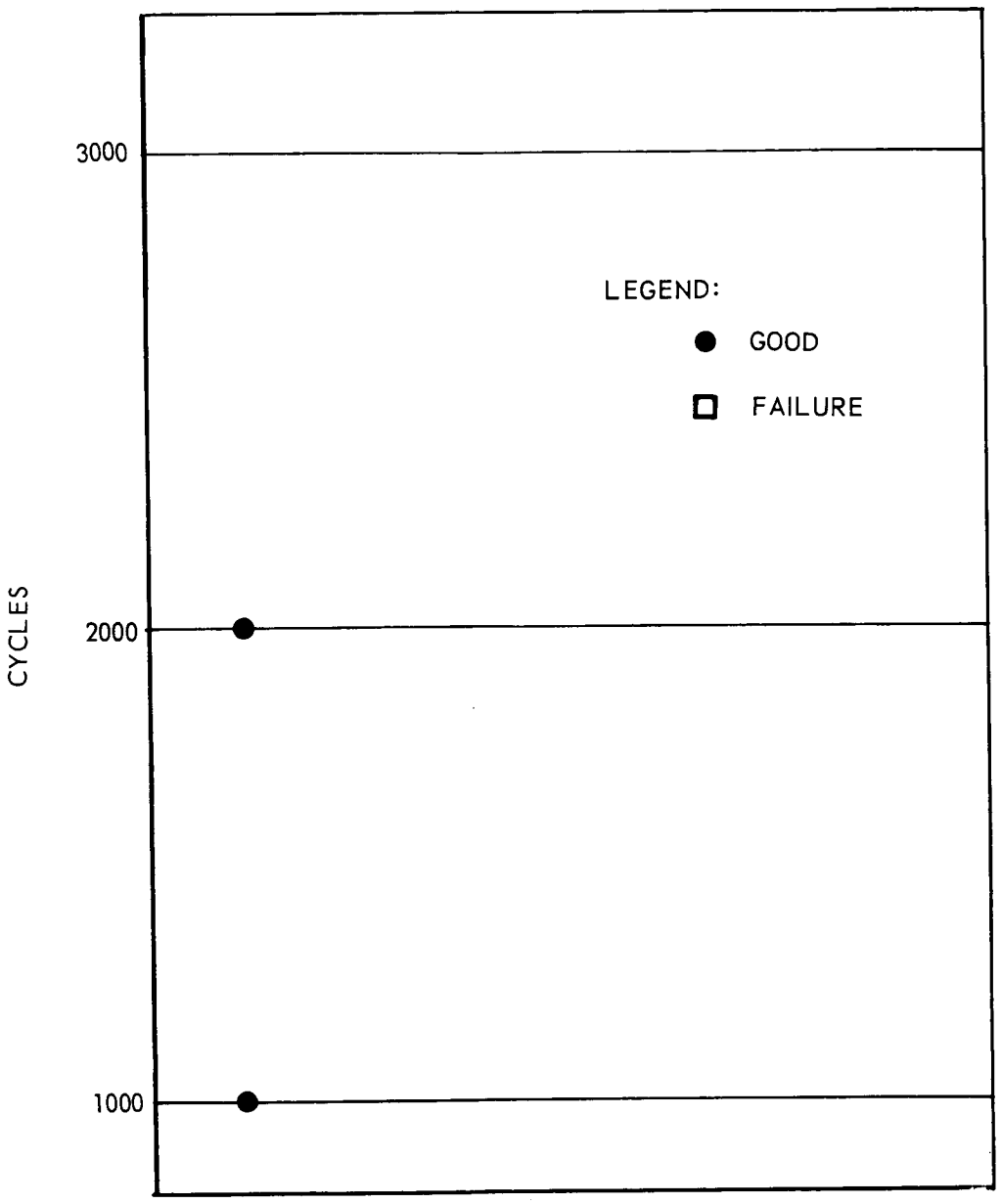


Figure 23. Twist-Flex Data -- Mylar T, 1/2-mil LN_2 Temperature, 4 in. x 2-3/4 in.

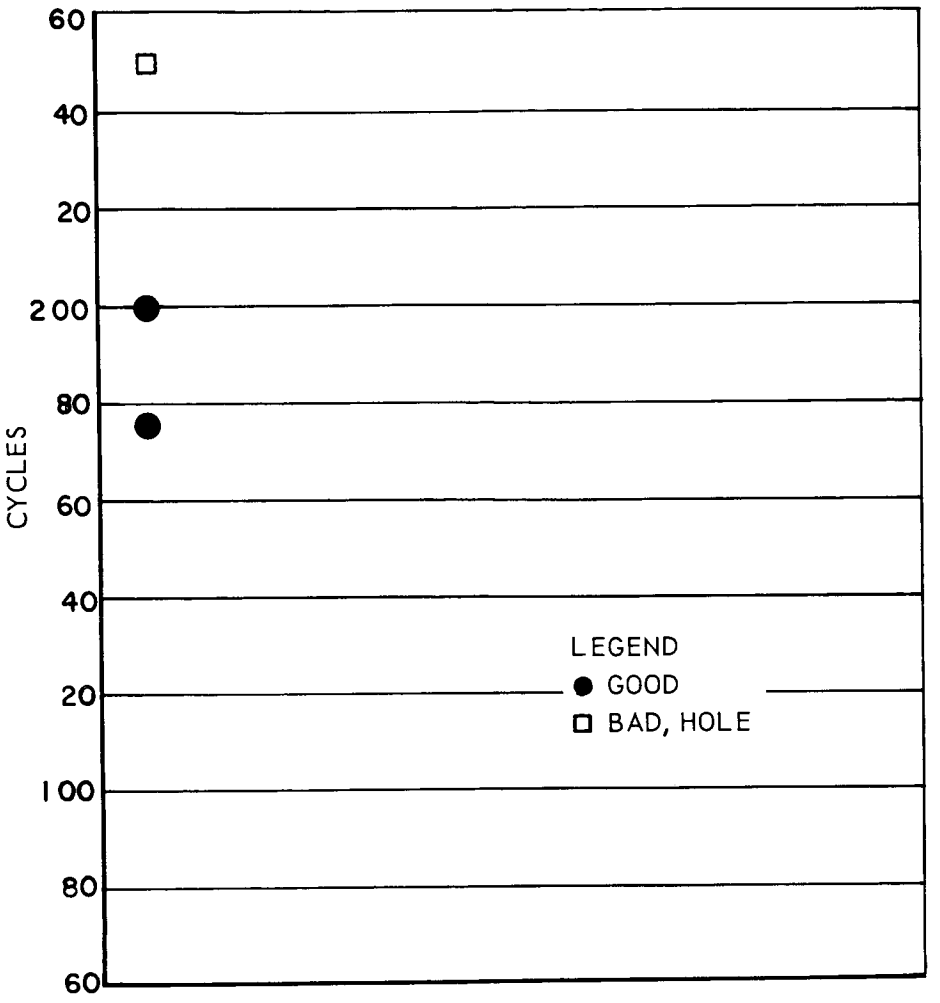


Figure 24. Twist-Flex Data -- Kapton Film, 1/2-Mil Room Temperature, 4 in. x 4 in.

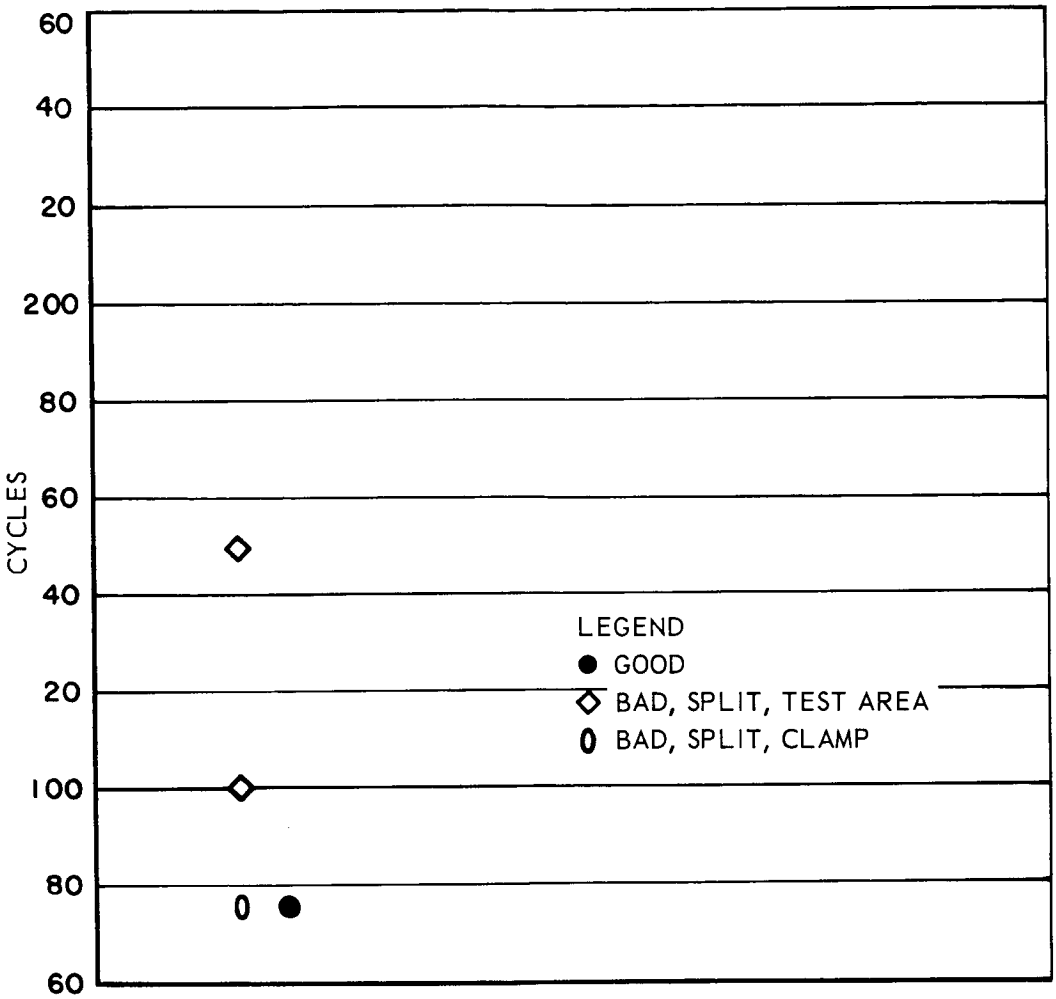


Figure 25. Twist-Flex Data -- Kapton Film, 1/2-Mil LN_2 Temperature, 4 in. x 4 in.

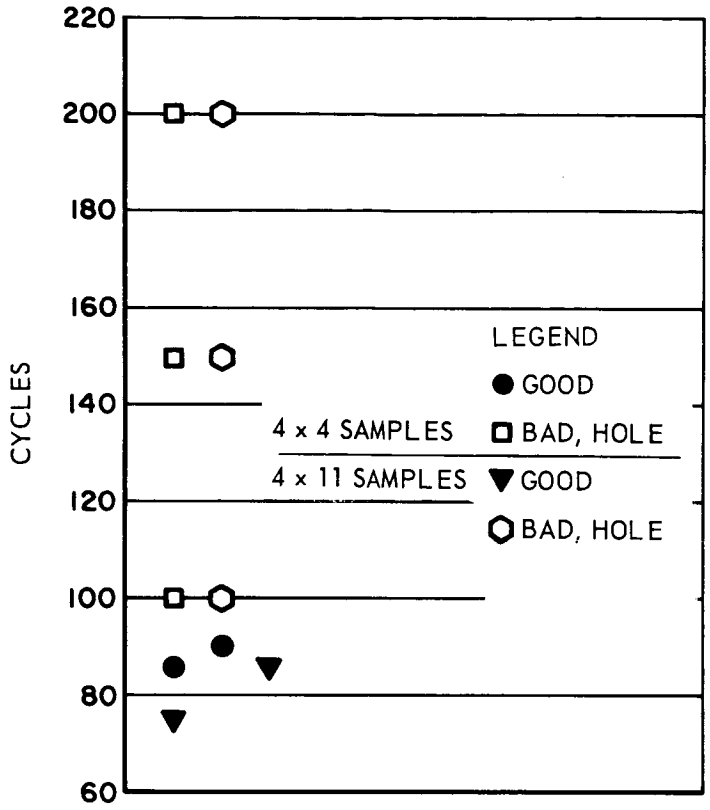


Figure 26. Twist-Flex Data -- Lexan, 1/2-Mil Room Temperature, 4 in. x 4 in. and 4 in. x 11 in.

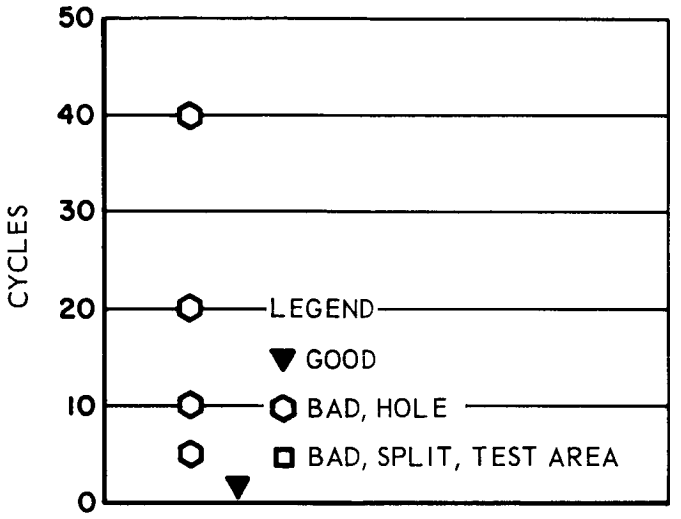


Figure 27. Twist-Flex Data -- Lexan, 1/2-Mil LN_2 Temperature, 4 in. x 11 in.

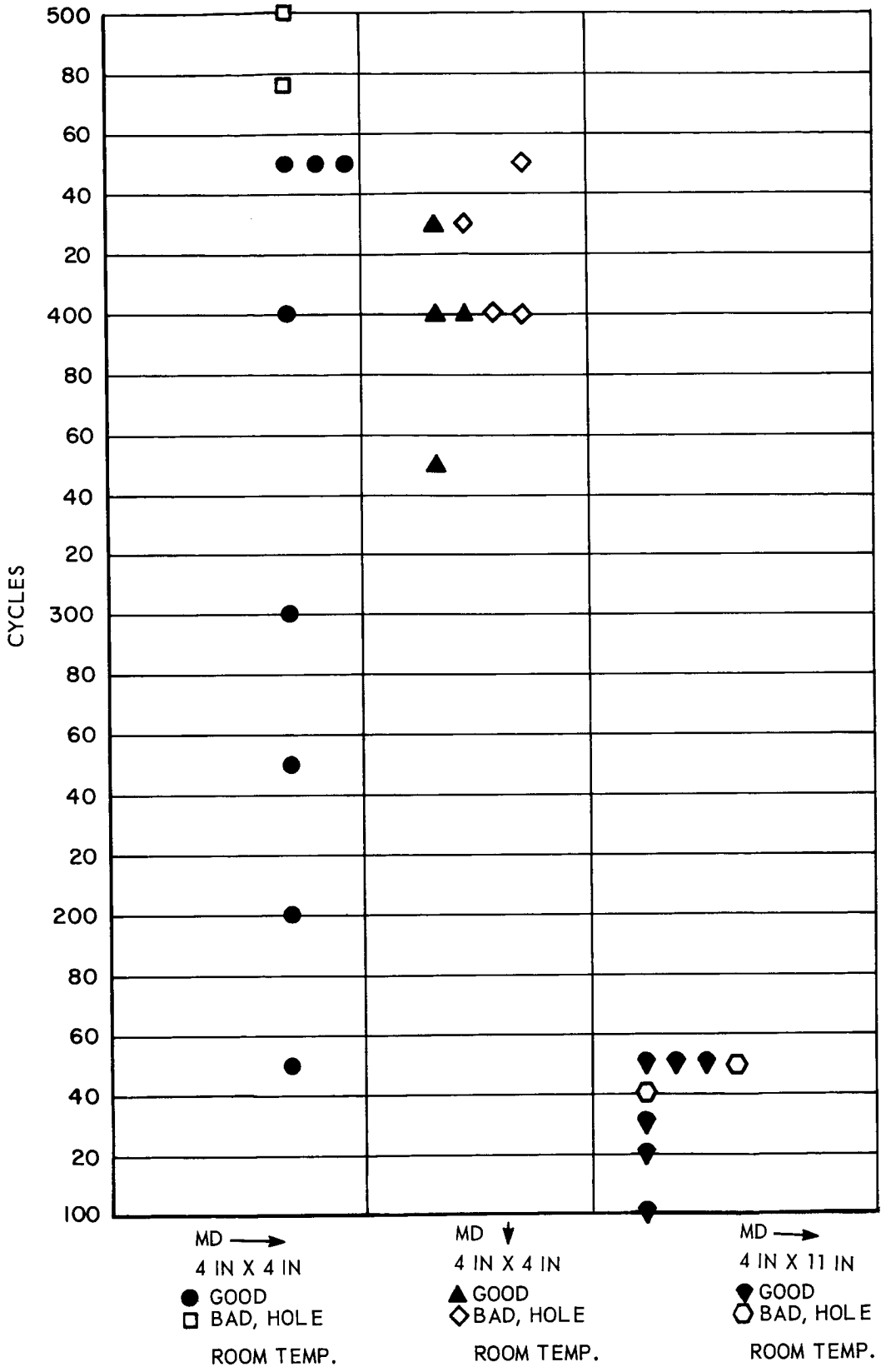


Figure 28. Twist-Flex Data -- Mylar T, 1/2-Mil Room Temperature, 4 in. x 4 in.

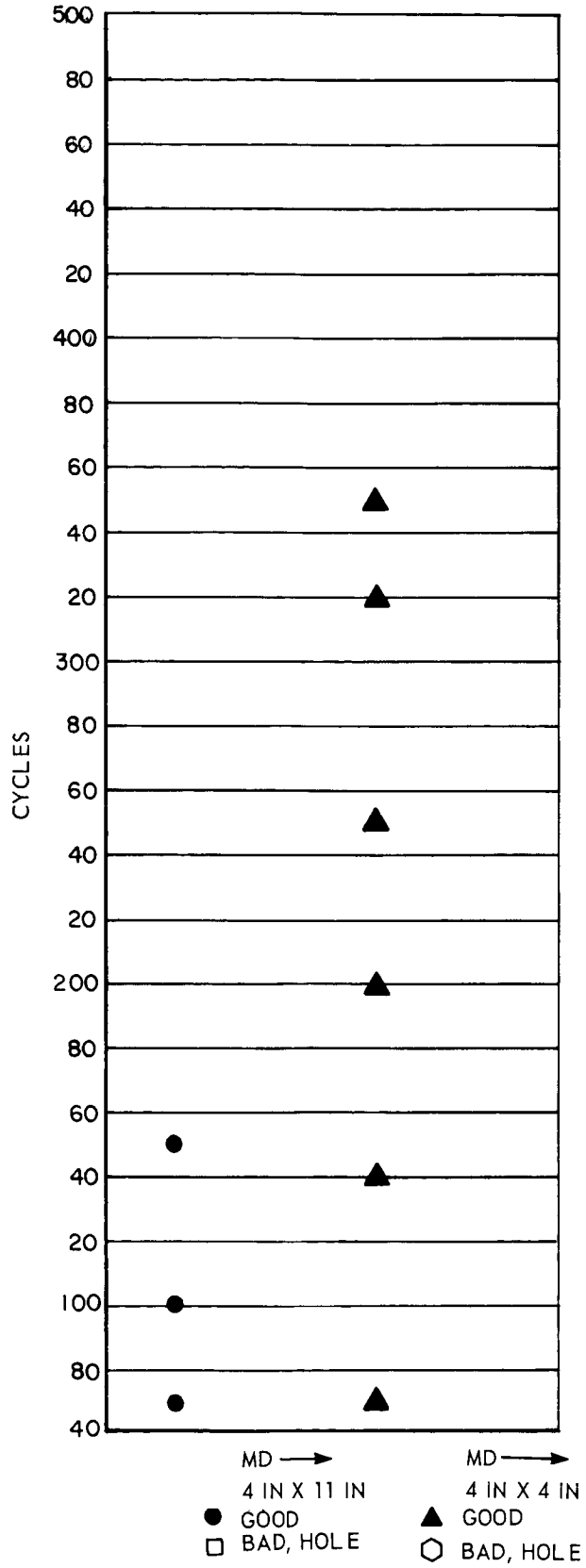


Figure 29. Twist-Flex Data -- Mylar T, 1/2-Mil LN_2 Temperature, 4 in. x 4 in. and 4 in. x 11 in.

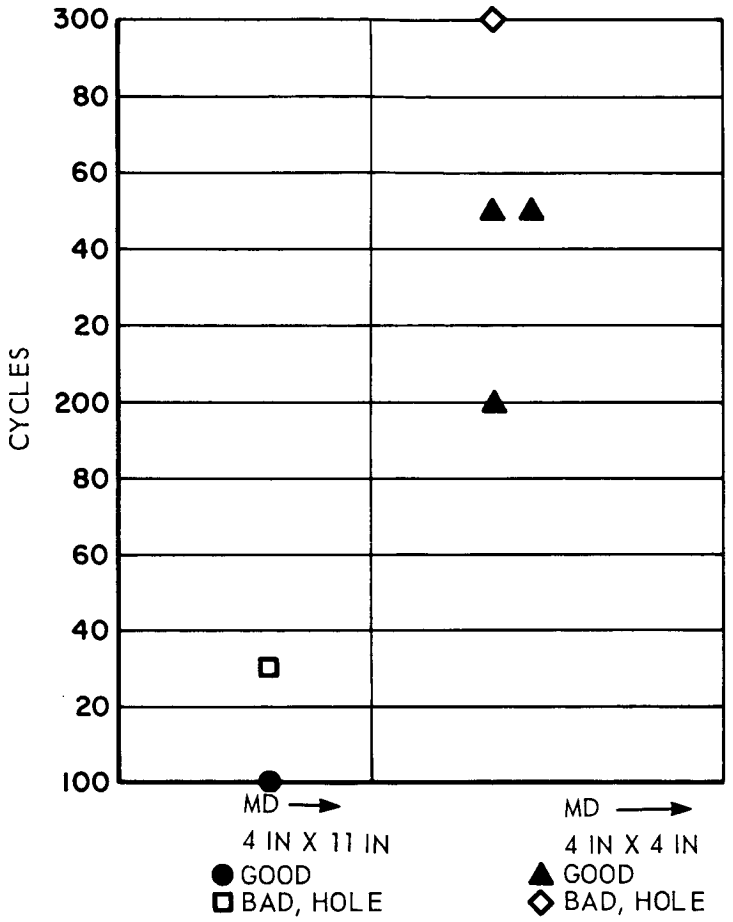


Figure 30. Twist-Flex Data -- Mylar T, 3/4-Mil, Room Temperature, 4 in. x 4 in. and 4 in. x 11 in.

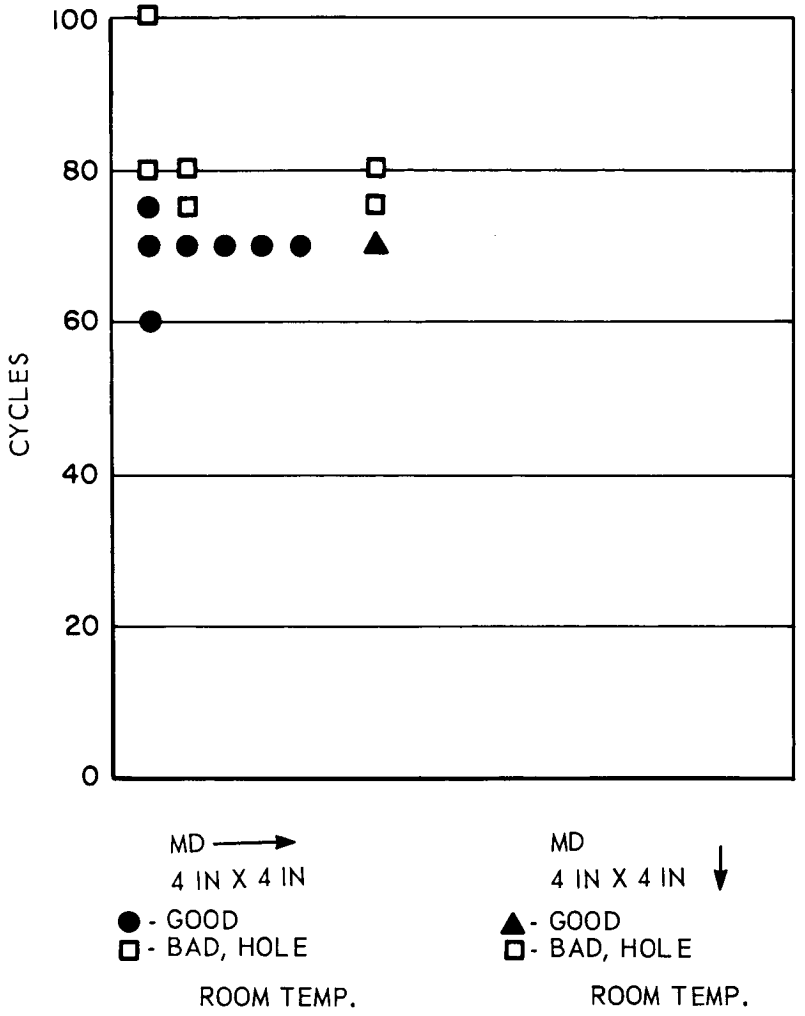


Figure 31. Twist-Flex Data -- Mylar A, 2-Mil Room Temperature, 4 in. x 4 in.

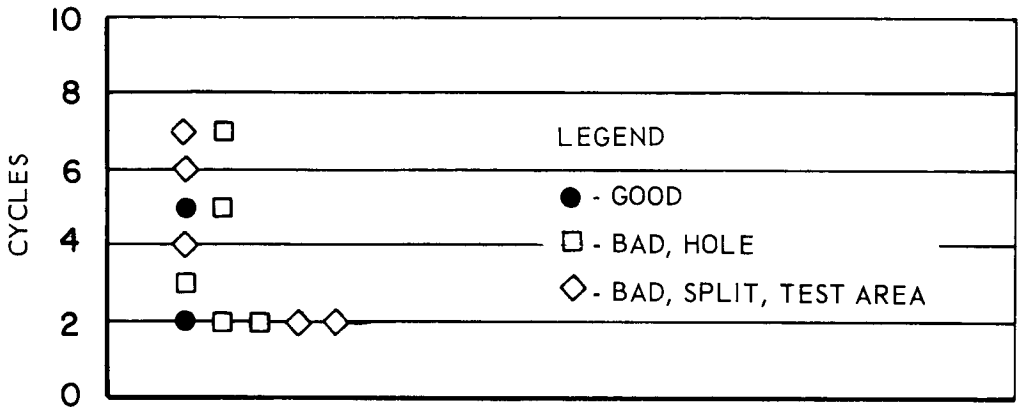


Figure 32. Twist-Flex Data -- Mylar A, 2-Mil LN_2 Temperature, 4 in. x 4 in.

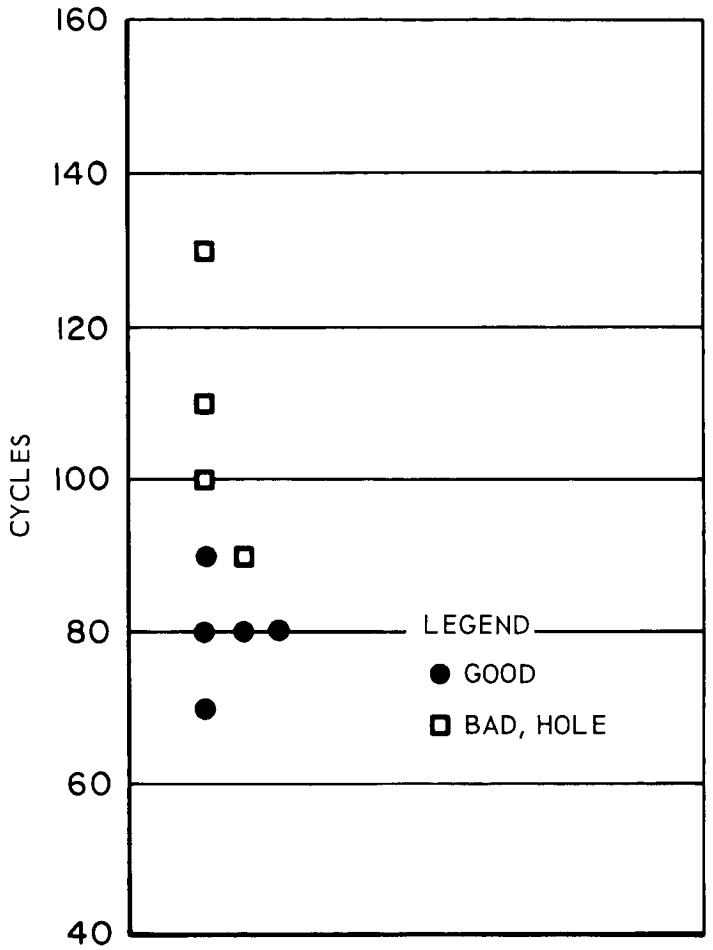


Figure 33. Twist-Flex Data -- Vitel VMF-414, 2-Mil Room Temperature, 4 in. x 4 in. MD→.

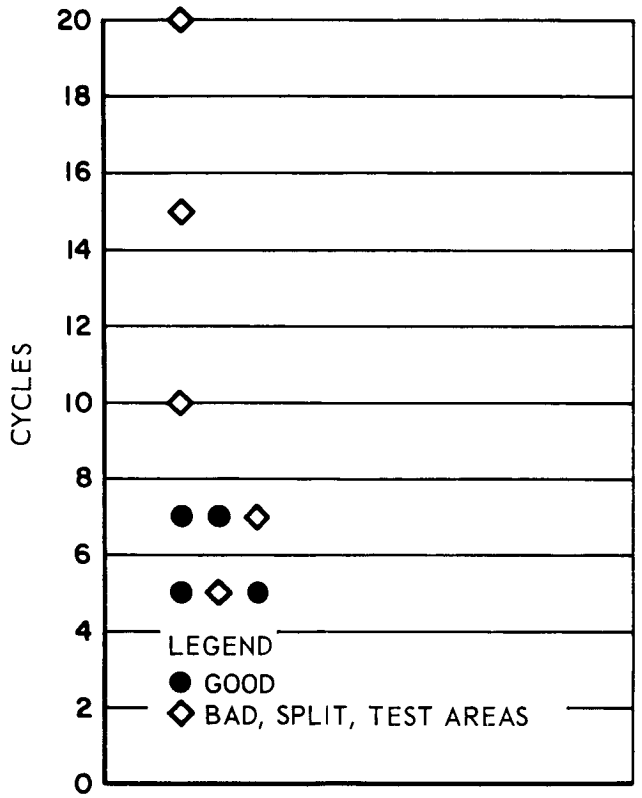


Figure 34. Twist Flex Data -- Vitel VMF-414, 2-Mil LN_2 Temperature, 4 in. x 4 in.

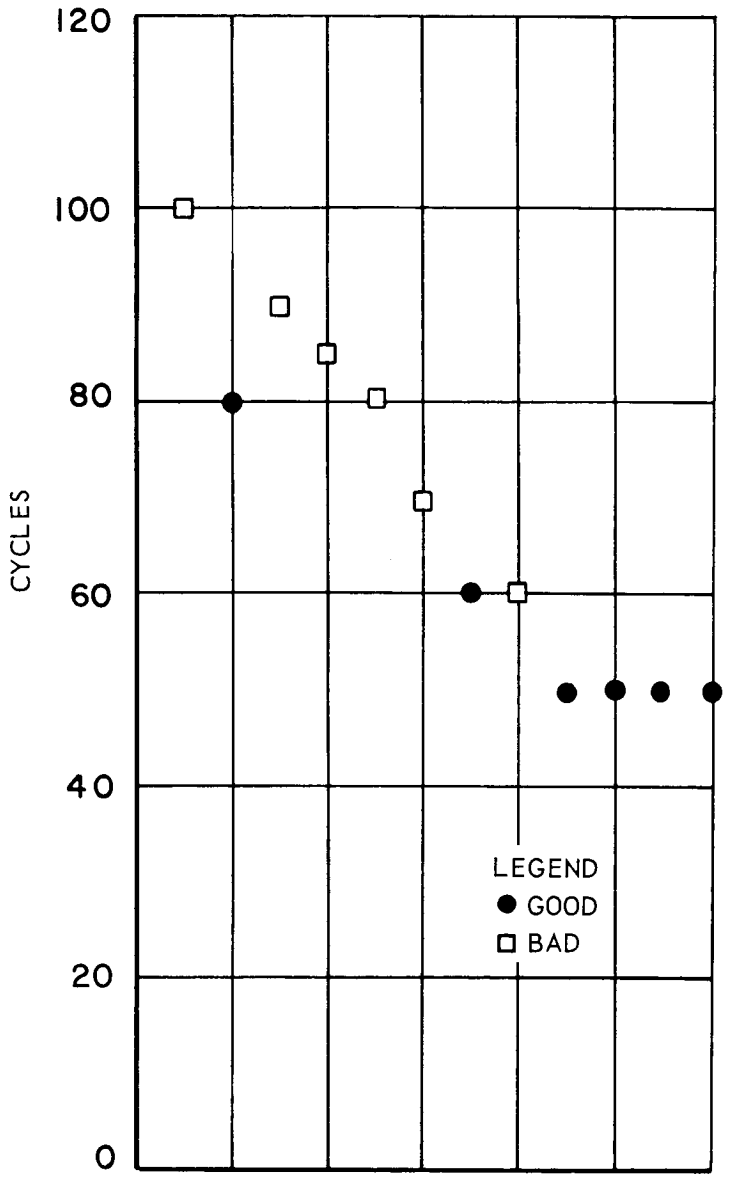


Figure 35. Twist-Flex Data -- Vitel VFR-338, 2-Mil Room Temperature, 4 in. x 4 in. MD→.

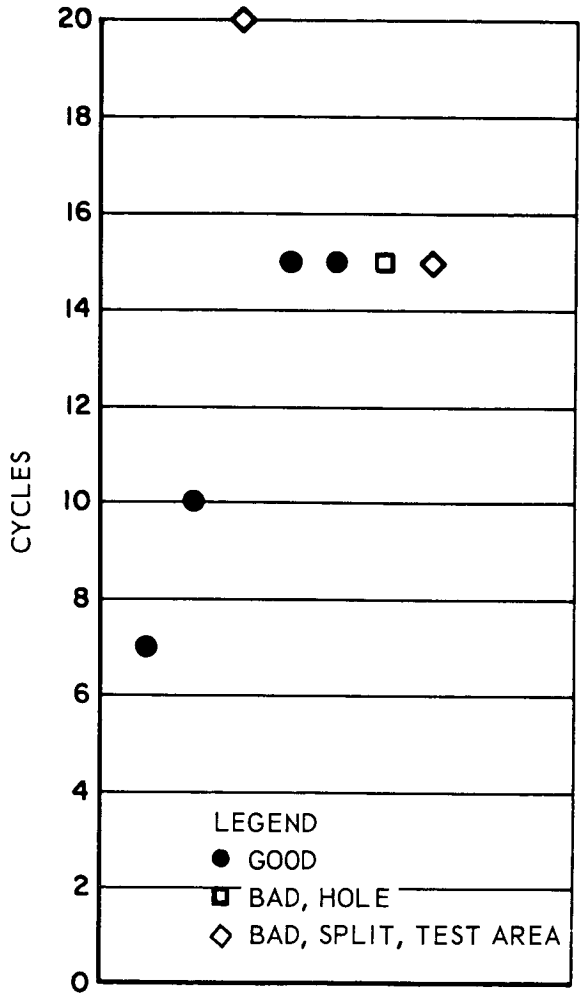


Figure 36. Twist-Flex Data -- Vitel VFR-338, 2-Mil LN_2 Temperature, 4 in. x 4 in. MD→.

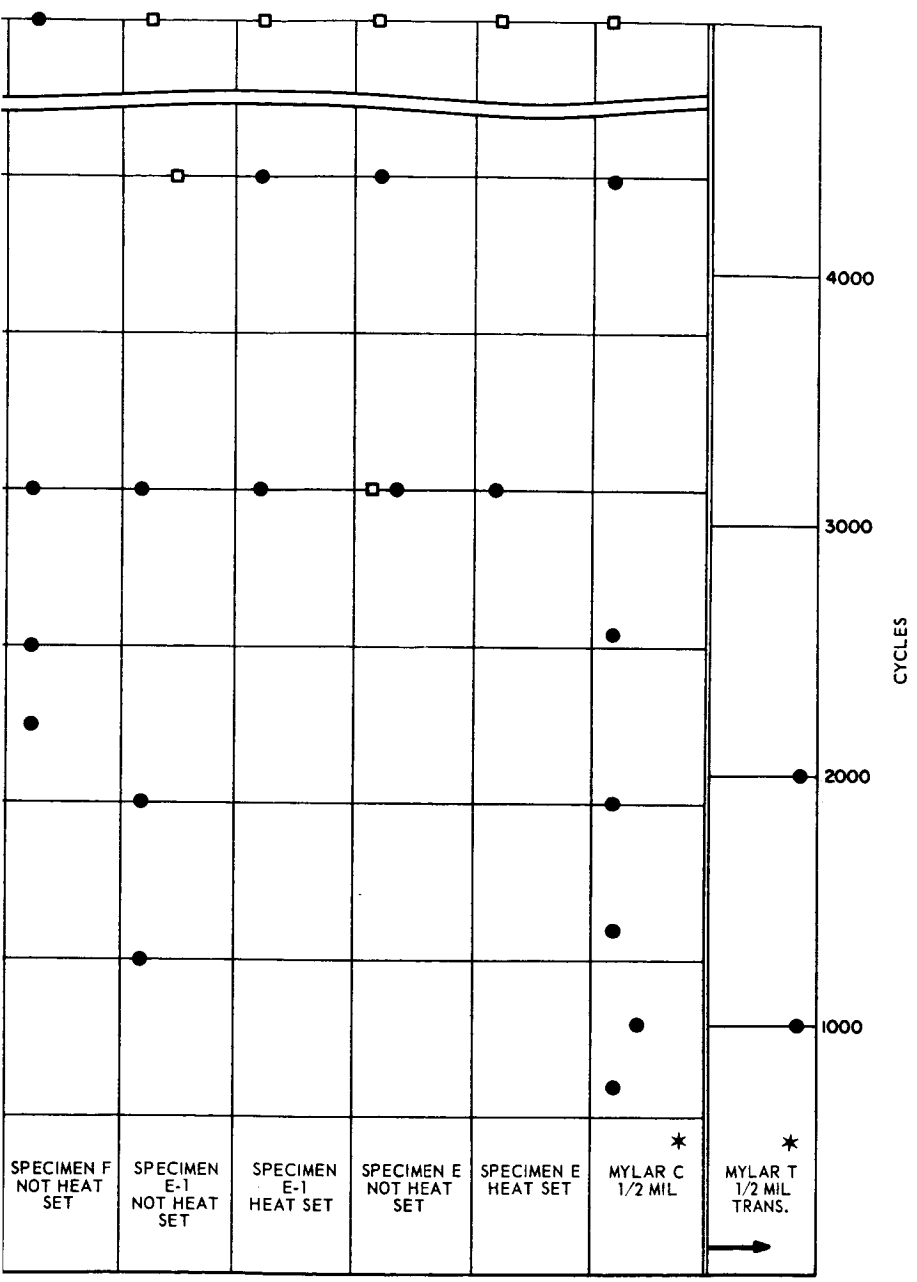


Figure 37. Twist-Fle
PET Film

34

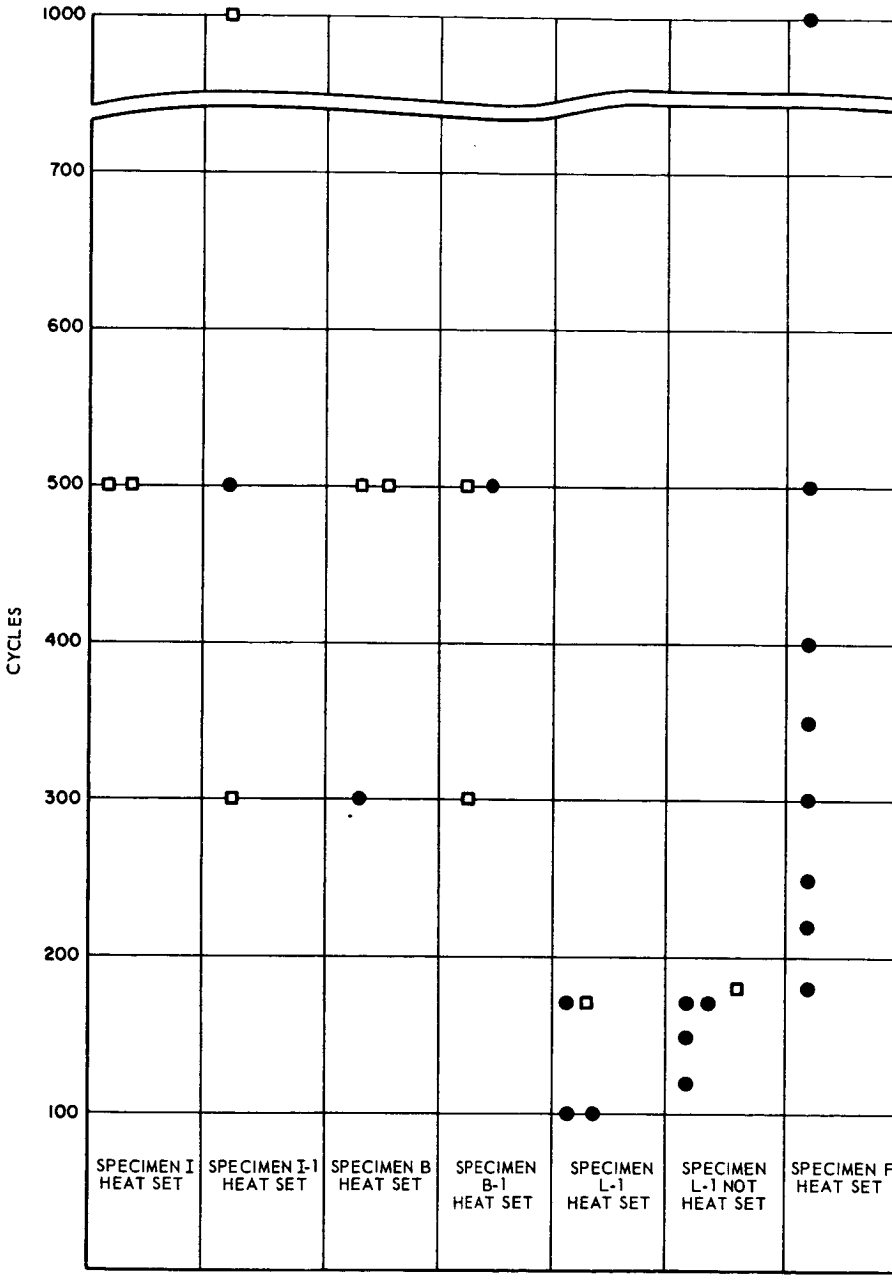
CODE:

SPECIMEN	STRETCH TEMPERATURE (°F)	STRETCH RATIO	STRETCH RATE (INCHES/MIN)	FILM THICKNESS (MILS)
I	200-208	2 X 2	0.5	0.1-0.4
I-1	200-208	2 X 2	8.0	0.2-0.4
B	168-176	2 X 2	0.5	0.3-0.5
B-1	168-176	2 X 2	8.0	0.5
L-1	200	3.5 X 3.5	8.0	0.4-0.7
L-1 (NOT HEAT SET)	200	3.5 X 3.5	8.0	0.5-0.8
F	170-175	4 X 4	0.5	0.5-1.0
F (NOT HEAT SET)	170-175	4 X 4	0.5	0.5-1.0
E-1(NOT HEAT SET)	168-172	3.5 X 3.5	8.0	0.3-0.8
E-1	168-172	3.5 X 3.5	8.0	0.5-0.7
E (NOT HEAT SET)	168-172	3.5 X 3.5	0.5	0.2-0.7
E	168-172	3.5 X 3.5	0.5	0.5

LEGEND:

- ● GOOD
- □ FAILURE
- ✶ DU PONT FILMS FOR COMPARISON

x Data -- Tennessee-Eastman Sequentially Biaxially Oriented
s, LN_2 Temperature, 4 in. x 2-3/4 in.


1000
700
600
500
400
300
200
100
CYCLES
SPECIMEN I HEAT SET
SPECIMEN I-1 HEAT SET
SPECIMEN B HEAT SET
SPECIMEN B-1 HEAT SET
SPECIMEN L-1 HEAT SET
SPECIMEN L-1 NOT HEAT SET
SPECIMEN F HEAT SET

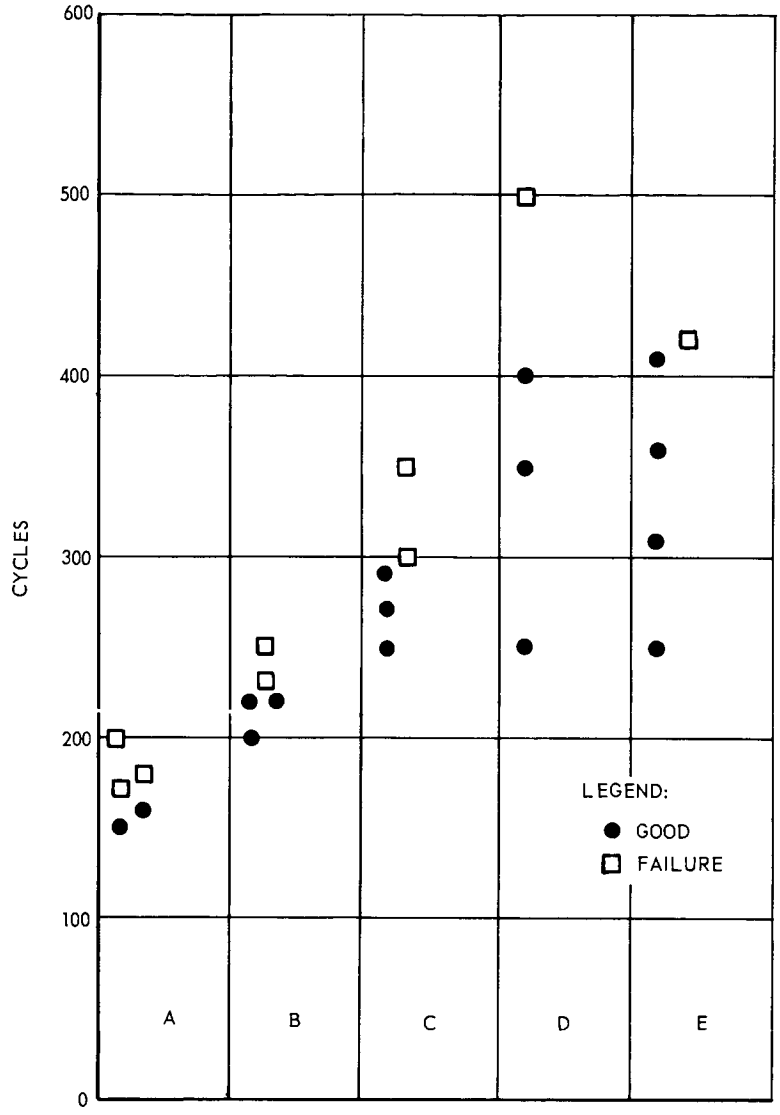
(2) Films which have been stretched 4 x 4 at 170-175°F, at a stretch rate of 0.5 inches per minute, are superior to Mylar C in twist-flex life at liquid nitrogen temperature. These films may be comparable to Mylar T in folding endurance, however, material available did not permit extensive testing; (see results on specimen F in figure 37 and compare with Mylar C and Mylar T in the same figure); (3) Films stretched 3.5 x 3.5 at about 200°F have poorer twist-flex endurance than those stretched 3.5 x 3.5 or 4 x 4 at about 170°F (Compare specimen L-1, stretched at about 200°F, with specimens E, E-1 and F, stretched at about 170°F, shown in figure 37); (4) Films stretched at about 170°F, at a stretch ratio of 3.5 x 3.5 or 4 x 4, have higher twist-flex endurance than those stretched 2 x 2. (Compare specimens E, E-1, F with specimens B, B-1 in figure 37(; (5) It appears that the stretch rate, either 0.5 inches per minute or 8.0 inches per minute, during biaxially orientation has little if any effect on the twist-flex life of PET films (Compare specimens E with E-1, B with B-1 and I with I-1 in figure 37).

In conclusion, the temperature of stretch and the degree of stretch each have a significant influence on the twist-flex life of PET films. The effect of heat setting is obscured by the fact that the film specimens not subjected to heat setting may have developed some crystallinity prior to testing, since approximately 2 months elasped before testing.

b. Twist-Flex Data for Simultaneously Biaxially Oriented PET Films

The twist-flex data obtained for the above indicated films are shown in figure 38. The following facts can be discerned from these data: (1) Heat-setting of simultaneously biaxially oriented PET films 10 sec. at 200°C has little or no effect on the twist-flex life of these films (compare specimens D and E in figure 38); (2) Films stretched at a ratio of 6 x 6 at 112°C yielded lower twist-flex performance than films stretched at a ratio of 4 x 4 at a temperature of either 91°C or 101°C (compare specimen A with specimen B, C, D, and E in figure 38); (3) Films stretched at a ratio of 4 x 4 at 101°C have greater twist-flex endurance than films stretched at a ratio of 4 x 4 at 91°C (compare specimens D and E with specimen B in figure 38); (4) None of the parameters covered in this sequential biaxial orientation study yielded films that performed as well as Mylar C in the twist-flex test at liquid nitrogen temperature (compare points in figure 38 with Mylar C in figure 37).

It appears therefore that the simultaneous method of biaxial orientation as carried out on the "hat-stretcher" does not yield films that compare in twist-flex performance to those prepared by the sequential method of biaxial orientation as carried out on the T.M. Long laboratory stretcher.



CODE:

SPECIMEN	STRETCH RATIO	STRETCH TEMPERATURE (°C)	HEAT SET CONDITIONS TIME (SEC)	HEAT SET CONDITIONS TEMP. (°C)	FILM THICKNESS (MILS)
A	6 X 6	112	10	200	0.5
B	4 X 4	91	10	200	0.8
C	4 X 4	101	30	200	0.8
D	4 X 4	101	—	—	0.75
E	4 X 4	101	10	200	0.85

Figure 38. Twist-Flex Data -- Simultaneously Biaxially Oriented PET Films, 4 in. x 2-3/4 in., LN_2 Temperature

c. Twist-Flex Data for Solvent Cast Poly (2,6-dimethylphenylene oxide) Films

PPO films were prepared by solvent casting PPO polymer (obtained from General Electric Co.) from 10 chloroform solution on glass plates.

The twist-flex data for these films is shown in figure 39.

2.4.5 The Twist-Flex Apparatus

The twist-flex apparatus used in determining the twist-flex life of films has been described.[1] The method used in determining the presence of failure points after twist-flex testing has not been previously described and is included below.

The film, after twist-flexing for a specific number of cycles, is clamped into a specially constructed film holder. This device allows the application of one pound of helium pressure to the bottom face of the film which is in a horizontal position. At the same time approximately one quarter inch of water is placed on the upper face of the film. Failure points in the film are determined by looking for bubbles of helium gas rising through the water layer. After removal of the film from the holder the failure point is marked with a wax pencil and identified as to type; i.e., hole, split, etc.

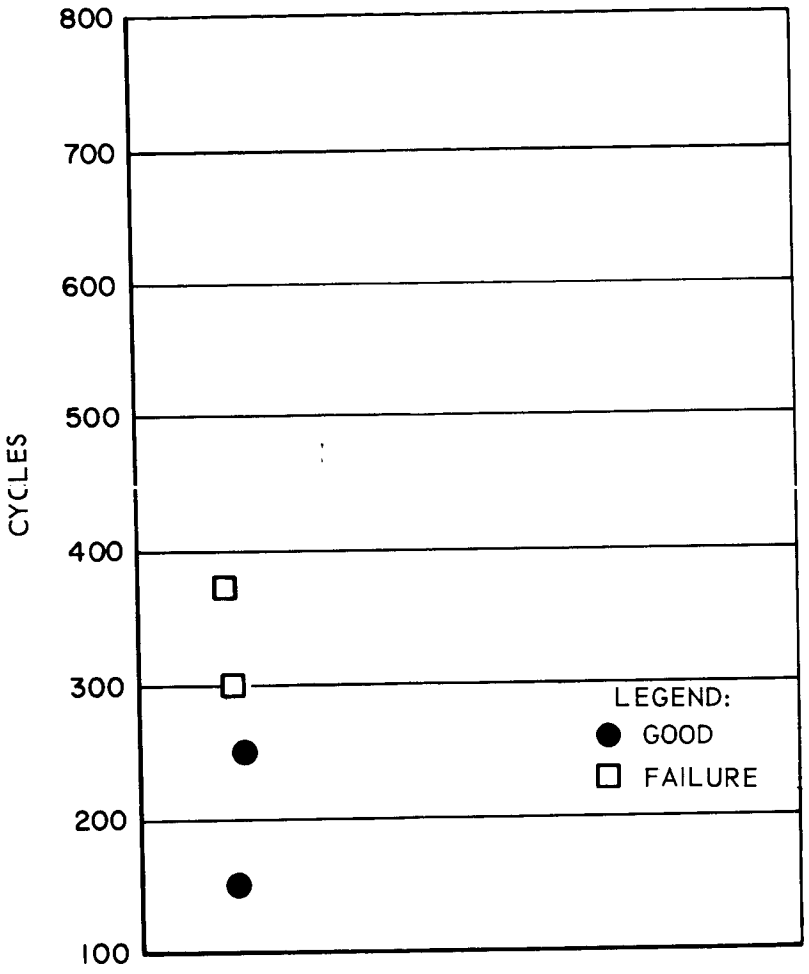


Figure 39. Twist-Flex Data -- Solvent Cast Poly (2,6-dimethylphenylene oxide) LN_2, 4 in. x 2-3/4 in., LN_2 (PPO) Film Thickness 0.7-1.5 Mils

2.5 Tensile Properties of Films

2.5.1 Tensile Properties of Various Commercially Available Polymeric Films

The following commercially available polymeric films were evaluated for tensile properties: Mylar types A, C, and T, Kapton (H-Film), Lexan, Vitel VMF-414 and Vitel VFR-338. These data are shown in table 1 and several of the film properties are summarized in table 2.

Mylar C

It is evident from the tensile, percent elongation, and modulus values in the M.D. (machine direction or longitudinal direction) and in the T.D. (transverse direction) that Mylar C is an almost balanced film, i.e., uniplanar isotropic orientation. That it is not completely balanced is evident from the somewhat greater tensile in the T.D. and corresponding greater modulus also in the T.D. (at 25°C), as shown in table 1.

On cooling to -195°C the tensile strength in the M.D. increases somewhat greater than that in the T.D. and is also evident for the modulus value. The change in percent elongation, on the other hand, is about the same in either direction. According to Heffelfinger and Schmidt (Preprint 32 b, Paper Presented at the Symposium on Effects of Molecular Orientation on Structure and Properties of Polymers, Part II, 53rd National Meeting A.I.Ch.E., May 1964), tensile strength is somewhat indicative of the perfection of orientation, elongation can be considered as a measure of the mobility of the chains under stress, and modulus is a measure of the stiffness of the film. On this basis, it would appear that at -195°C molecular orientation increases somewhat faster in the M.D. than in the T.D., and so does the modulus. This might be interpreted to mean that the shrinkage of the film is greater in the M.D. Presumably this shrinkage occurs in the amorphous regions between crystallites, and possibly because of the greater coiling of the gauche forms of PET. It is also possible that some of the extended trans forms in the amorphous region are isomerizing to the more stable gauche forms. This is of course quite speculative but provides a possible working model upon which to base further investigations on the "nature" of the rigid lattice.

Mylar-T

According to Heffelfinger and Schmidt (op. cit.) restretching of two-way stretched PET film in the original (M.D.) direction results in a marked extension of the amorphous structure with an attendant decrease in density (table 3). If we assume Mylar-T to be Mylar-C which has been post-stretched in the M.D., then the decrease in density is in accord with Hefflfinger's and Schmidt's paper. Following their thinking, the additional stretch results in the molecular chain segments in the amorphous regions being drawn "taut". That is, some of the gauche forms are converted to the trans forms in the amorphous regions, and many of the chain segments are limited in movement due

TABLE 1. TENSILE PROPERTIES OF SEVERAL COMMERCIAL FILM MATERIALS

Material	Direction	Temp. °C	Ult. Tensile	Yield, .2% Offset	Elongation %	Modulus
Mylar-T	Longitudinal	25	43,000	20,500	20	680,000
			40,000	20,000	25	580,000
			38,000	20,000	25	600,000
		(Mean)	40,330	20,000	24	620,000
Mylar-T	Longitudinal	-195	58,500	52,000	7.5	900,000
			56,000	47,000	8.0	800,000
		(Mean)	57,250	50,000	7.75	850,000
Mylar-T	Transverse	25	20,500	13,000	75	300,000
			21,000	13,000	85	310,000
			19,000	12,000	93	330,000
		(Mean)	20,166	12,666	84	315,000
Mylar-T	Transverse	-195	53,000		5.0	960,000
			57,000		4.5	1,240,000
		(Mean)	55,000		4.75	1,100,000
Lexan	Longitudinal	25	8,500	8,000	20	180,000
			8,000	8,000	40	120,000
			8,000	8,000	13	130,000
		(Mean)	8,167	8,000	24	143,334
Lexan	Longitudinal	-195	46,000		6	900,000
			47,500		5	900,000
		(Mean)	46,750		5.5	900,000
Lexan	Transverse	25	8,200	7,400	8	160,000
			8,000	8,000	10	163,000
			8,200	7,600	13	144,000
		(Mean)	8,134	7,534	10	155,667
Lexan	Transverse	-195	40,000		4	900,000
			40,500		4	900,000
		(Mean)	40,250		4	900,000

TABLE 1. (Cont.) TENSILE PROPERTIES OF SEVERAL COMMERCIAL FILM MATERIALS

Material	Direction	Temp. °C	Ult. Tensile	Yield .2 % Offset	Elongation %	Modulus
Kapton	Longitudinal	25	20,000	14,000	24	200,000
			26,500	15,000	41	300,000
			25,000	15,000	26	280,000
		(Mean)	23,834	14,667	31	260,000
Kapton	Longitudinal	-195	48,000		5	800,000
			33,000		5	620,000
		(Mean)	40,500		5	710,000
Kapton	Transverse	25	22,000	13,000	26	240,000
			23,500	15,000	24	220,000
		(Mean)	22,750	14,000	22	230,000
Kapton	Transverse	-195	36,500		6	580,000
			27,500		3	700,000
		(Mean)	32,000		4.5	640,000
Mylar-C	Longitudinal	25	22,000	15,000	115	410,000
			20,500	15,000	90	380,000
			19,500	15,000	72	410,000
		(Mean)	20,333	15,000	92.5	400,000
Mylar-C	Longitudinal	-195	47,500	45,000	7	700,000
			49,200	45,000	7	800,000
		(Mean)	48,350	45,000	7	750,000
Mylar-C	Transverse	25	24,000	15,000	85	470,000
			22,500	14,500	85	440,000
			24,500	14,000	100	450,000
		(Mean)	23,333	14,333	90	453,300
Mylar-C	Transverse	-195	46,500	42,000	6.5	760,000
			48,500	42,500	7.5	700,000
		(Mean)	47,500	42,250	7.0	730,000

TABLE 1. (Cont.) TENSILE PROPERTIES OF SEVERAL COMMERCIAL FILM MATERIALS

Material	Direction	Temp. °C	Ult. Tensile	Yield, .2 % Offset	Elongation %	Modulus
Mylar A 2 Mil	Longitudinal	25	26,000	14,500	127	420,000
			21,000	14,500	65	440,000
		(Mean)	23,500	14,500	96	430,000
Mylar A 2 Mil	Transverse	25	20,500	14,500	85	420,000
			22,500	14,000	120	400,000
			23,500	14,000	130	410,000
		(Mean)	22,167	14,167	112	410,000
VMF 414 2 Mil	Longitudinal	25	22,300	13,000	150	380,000
			22,500	13,000	153	360,000
		(Mean)	22,400	13,000	152	370,000
VMF 414 2 Mil	Transverse	25	24,500	15,000	120	460,000
			———	14,500	———	450,000
		(Mean)	24,500	14,750	120	455,000
VFR 338 2 Mil	Longitudinal	25	25,800	13,000	110	390,000
			26,000	13,500	108	400,000
		(Mean)	25,900	13,250	109	395,000
VFR 338 2 Mil	Transverse	25	26,700	14,000	103	400,000
			27,300	14,000	109	410,000
		(Mean)	27,000	14,000	106	405,000

TABLE 2. SUMMARY OF PROPERTIES FOR FILMS OF MYLAR -C, AND T, LEXAN AND KAPTON (H-FILM)

Polymer Film	Mylar-T	Mylar-C	Kapton	Lexan
Tensile at 25° in M.D.	40,300	20,300	23,800	8,200
at -195° in M.D.	57,300	48,350	40,500	46,800
% Increase in Tensile in M.D.	42	138	70	470
Tensile at 25° in T.D.	20,200	23,300	22,800	8,100
at -195° in T.D.	55,000	47,500	32,000	40,300
% Increase in Tensile in T.D.	172	104	50	400
% Elongation at 25° in M.D.	24	92.5	31	24
at -195° in M.D.	7.8	7.0	5	5.5
% Decrease in % Elongation in M.D.	63	93	84	77
% Elongation at 25° in T.D.	84	90	22	10
at -195° in T.D.	4.8	7	4.5	4
% Decrease in % Elongation in T.D.	94	92	80	60
Modulus at 25° in M.D.	620,000	400,000	260,000	143,000
at -195° in M.D.	850,000	750,000	710,000	900,000
% Increase in Modulus	37	88	173	530
Modulus at 25° in T.D.	315,000	453,000	230,000	156,000
at -195° in T.D.	1,100,000	730,000	640,000	900,000
% Increase in Modulus in T.D.	250	61	178	478
Twist-Flex Life at 25°C, 4" x 4", 0.5 mil	>400	Ca: 260	Ca:225	Ca:90
at -195°C 4" x 4", 0.5 mil	>350	Ca: 75	Ca: 75	Ca:12

TABLE 3. CRYSTALLINITY AND ISOMER DISTRIBUTION IN MYLAR-C AND T[1]

	Mylar-C	Mylar-T
Density	1.400	1.385
% Crystallinity	48	42
% Trans in Cryst. Region	48	42
% Trans in Amorp. Region	26	46
% Gauche in Amorp. Region	26	12
Crystallite Length (Å)	64	56
Amorphous length (Å)	56	85

[1] Based on papers by Heffelfinger and Schmidt, op. cit.; Daubeny, Bunn, and Brown, Proc. Roy. Soc. (London), 226A, 531 (1964); and Johnson, J. Appl. Polymer Sci., 2, 205 (1959)

to entanglements (persisting from the original amorphous or random oriented state) with other taut chains or crystallites. In this state the benzene rings are approximately parallel with the plane of the film. Slippage of one trans molecule over another is presumably thus enabled when mechanical force is applied.

In examining the mechanical properties of Mylar-T (table 2), the unbalanced or anisotropic behavior of the film is apparent. Thus, at 25°C, the tensile strength and modulus values are greater in the M.D., while the percent elongation is less in the M.D. These results are in accord with the observations of Heffelfinger and Schmidt that post-stretching results in producing additional "taut" trans forms of PET in the amorphous regions (from the gauche forms). In addition it is evident that the tensile strength and modulus values are less than that of Mylar-C in the T.D. This suggests that the orientation and stiffness have been reduced in the transverse direction to attain the greater orientation and stiffness in the machine direction. This might be due to some disentanglement of gauche or amorphous trans structures with themselves or with the crystallites. Also, the additional stretching probably contributes to orienting the benzene rings, particularly in the trans forms, more coplanar with the film surface. The lower elongation in the T.D., as well as in the M.D., for Mylar-T vs. Mylar-C is undoubtedly due to more "taut" trans structures in the amorphous regions of the former polymer.

At -195°C, the tensile strength and modulus values increase in each direction; the increase in tensile strength and modulus values in the transverse direction in each case being rather noteworthy but not necessarily unexpected. In particular, one might expect less shrinkage in the case of Mylar-T than Mylar-C because of the greater total amount of the extended trans structure. Moreover, at -195°C, for a more "ordered" structure such as Mylar-T one would expect the molecular interactions between layers of chains to exceed the thermal energy contributing to their motions (if any) at -195°C.

The interesting feature of Mylar-T concerns its percent elongation at -195°C, in particular, the M.D. now has a greater percent elongation than the T.D. (whereas at 25°C the transverse direction has the greater elongation as is expected). As suggested above, at -195°C we are dealing with a rigid lattice where the intermolecular energy of attraction (van der Waals or dispersion forces) exceed the thermal energy kT. Accordingly, the application of force in the machine direction might be able to extend some of the gauche forms more readily in the amorphous regions between crystallites than a force in the transverse direction which requires pulling apart close layers (lamellae) of extended trans chains in a rigid lattice. At 25°C, on the other hand, where kT exceeds the molecular interaction energy between planes of chains, a force in the transverse direction can evidently more readily separate layers of molecules than extend them (the gauche forms) longitudinally in the machine direction.

2.5.2 Tensile Properties of Experimental Films

a. Tensile Properties of Sequentially Biaxially Oriented PET Films

Shown in table 4 are the tensile strength properties determined for the indicated films. The following conclusions can be drawn concerning the effect of sequential biaxial orientation parameters on the tensile strength properties of the resultant films at liquid nitrogen temperature. (1) In several cases measurements were made on films in two directions. These were designated as "A" and "B" directions. These measurements showed that the films were not nearly as balanced in orientation as is Mylar C. For example, see ultimate tensile strength properties for G-1, heat set and not heat set, "A" and "B" directions. (2) Heat setting has a pronounced effect on ultimate tensile strength, yield and percent elongation values but not nearly as great an effect on modulus. For example see the G-1 series in table 4 where in the "A" direction ultimate tensile was 46,100 psi before heat setting and 35,950 psi after heat setting; similarly in the "B" direction the values were 62,166 psi and 45,600 psi respectively. Values for yield strength in the "A" direction were 38,000 psi before heat setting and 29,000 psi after heat setting; in the "B" direction the values were 48,500 psi and 27,500 psi respectively. Thus it can be seen that in each case heat setting has served to decrease the values of ultimate tensile strength, yield and percent elongation. This trend can also be seen in the L-1 series of specimens in table 4, where heat setting has served to decrease the three tensile strength properties at liquid nitrogen temperature. Since heat setting serves to increase crystallinity it can be seen that ultimate tensile strength, yield and elongation properties are related to and probably dependent on the crystallinity level of the film. (3) Ultimate tensile strength properties of heat set films at liquid nitrogen temperature are markedly dependent on the stretch ratio. Out of nine heat set films tested it was found that those stretched 3.5 x 3.5 and 4 x 4 had ultimate tensile strength values considerably higher than those stretched at lower ratios. This can be seen in specimens F, G-1 ("B" direction) and L-1 where ultimate tensile strength values were in the range of 45,600 psi to 52,000 psi and in specimens B, B-1, K-1, I and I-1 where ultimate tensile strength values were only 11,000 psi to 29,550 psi. This latter group had been stretched at ratios of 2 x 2 and 3 x 3. This trend is not seen in the yield strength, percent elongation and modulus values of these film specimens. (4) Tensile strength properties at liquid nitrogen temperature of not-heat-set-films are not changed greatly by twist-flexing 220 cycles at liquid nitrogen temperature. This can be seen in specimens G-1 (not heat set, "B" direction) before and after twist-flexing for 220 cycles at liquid nitrogen temperature.

b. Tensile Strength Properties of Simultaneously Biaxially Oriented PET Films

The tensile strength properties of the above indicated films are shown in table 5. The following conclusions can be drawn from these data.

TABLE 4. TENSILE PROPERTIES OF SEQUENTIALLY BIAXIALLY ORIENTED PET FILMS

Material	Direction	Temp.	Ult. Tensile	Yield at .2% Offset	Elongation %	Modulus
L-1(Heat Set)		LN_2	47,500	42,000	5.2	840,000
			50,000	42,000	6.0	600,000
		Mean	48,750	42,000	5.6	720,000
L-1(Not Heat Set)		LN_2	56,000		6.0	1,000,000
			62,000			
			57,000	52,000	6.5	980,000
		Mean	58,300	52,000	6.25	990,000
K-1(Heat Set)		LN_2	23,500	21,000	6.0	450,000
			28,500	25,000	6.0	550,000
		Mean	26,000	23,000	6.0	500,000
F(Heat Set)		LN_2	44,200	42,000	5.5	850,000
			59,800	46,500	11.0	850,000
		Mean	52,000	44,250	8.3	850,000
G-1(Heat Set)	"A"	LN_2	34,400	30,000	6.8	1,020,000
			37,500	28,000	13.5	700,000
		Mean	35,950	29,000	10.2	860,000
G-1(Heat Set)	"B"	LN_2	33,000	23,500	6.0	640,000
			55,000	31,500		1,300,000
			49,000			
		Mean	45,600	27,500	6.0	970,000
G-1(Not Heat Set)	"A"	LN_2	47,000			700,000
			44,700	38,000	30.0	680,000
			46,500	38,000	13.0	820,000
		Mean	46,100	38,000	21.5	733,000
G-1(Not Heat Set)	"B"	LN_2	63,500		5.3	1,600,000
			51,000	37,000	4.0	1,400,000
			72,000	60,000	5.0	1,400,000
		Mean	62,166	48,500	4.6	1,466,667
G-1(Not Heat Set) (Flexed 220 cycles in LN_2)	"B"	LN_2	75,000		6.8	1,800,000
			65,000	57,000	5.5	1,320,000
			66,000	56,000	4.5	1,300,000
		Mean	68,667	56,500	5.6	1,473,000
I-1(Heat Set)		LN_2	18,500		3.0	540,000
			22,000		6.0	
			22,500		4.0	620,000
		Mean	21,000		4.3	580,000
I(Heat Set)		LN_2	11,200		4.0	320,000
			10,800		2.5	228,000
		Mean	11,000		3.3	274,000
B-1(Heat Set)		LN_2	30,400		6.0	480,000
			28,800		6.0	450,000
		Mean	29,500		6.0	465,000
B(Heat Set)		LN_2	25,400	24,200	7.0	400,000
			25,800	24,000	6.7	380,000
		Mean	25,600	24,100	6.9	390,000

TABLE 4 (Cont). TENSILE PROPERTIES OF SEQUENTIALLY BIAXIALLY ORIENTED PET FILMS

Code:

Specimen	Stretch Temperature (°F)	Stretch Ratio	Stretch Rate (Inches/Minute)
C-1	198-204	4 x 4	8.0
I-1	200-208	2 x 2	8.0
I	200-208	2 x 2	0.5
B-1	168-176	2 x 2	8.0
B	168-176	2 x 2	0.5
I-1	200	3.5 x 3.5	8.0
K-1	200	3 x 3	8.0
F	170-175	4 x 4	0.5

TABLE 5. TENSILE STRENGTH PROPERTIES OF SIMULTANEOUSLY BIAXIALLY ORIENTED PET FIIMS

Material	Temperature	Ultimate Tensile Strength	Yield at .2% Offset	Elongation %	Modulus
4X Drawn at 101°C, heat set 10 seconds at 200°C	LN_2	90,500		43.5	
		82,000	53,000	24.3	1,260,000
		65,000	40,000	12.0	820,000
	Mean	79,167	46,500	26.6	1,040,000
4X Drawn at 91°C, heat set 10 seconds at 200°C	LN_2	74,000	48,000	35.0	1,100,000
		73,000	45,000	37.0	1,000,000
	Mean	73,500	46,500	36.0	1,050,000
4X Drawn at 101°C, heat set 30 seconds at 200°C	LN_2	69,000	40,000	34.0	1,140,000
		53,000	32,000	31.5	840,000
		50,000	32,000	22.0	880,000
	Mean	57,333	34,667	29.2	953,333
4X Drawn at 101°C, not heat set	LN_2	46,000		10.5	
		44,500		5.0	800,000
		51,000	38,000	9.5	740,000
	Mean	47,167	38,000	8.3	770,000
6X Drawn at 112°C, heat set 10 seconds at 200°C	LN_2	57,000		27.5	
		55,000	42,000	21.0	860,000
		51,000	39,000	14.0	800,000
	Mean	54,333	40,500	20.8	830,000

(1) Ultimate tensile strength properties in general are considerably greater in all the films tested in this group than those in the sequentially oriented PET group of films. There are no obvious trends in the ultimate tensile strength values as a function of their orientation parameters.

(2) The percent elongation values for this group of films are in general considerably greater than in the sequentially oriented PET films. Again, there are no obvious trends discernible as a function of orientation parameters.

In general, the scatter of values between multiple determinations on the same specimen is greater than that found in the other groups tested and points up the greater inhomogeniety of these films.

c. Tensile Strength Properties of Other Film Materials

Shown in table 6 are the tensile strength properties of several other film materials. These include solvent cast poly(2,6-dimethyl phenylene oxide) films (PPO), solvent cast poly(ethylene isophthalate) films and simultaneously biaxially oriented (hat-stretched) poly(ethylene isophthalate) films.

The ultimate tensile strength, percent elogation and modulus values of all these films were extremely low in comparison to the various commercial and experimental films tested in this program. A comparison between solvent cast and "hat-stretched" poly(ethylene isophthalate) films shows that the "hat-stretched" films had somewhat higher ultimate tensile strength and percent elogation values but considerably lower modulus than the solvent cast film.

The reason for the generally lower values for tensile strength properties in this group as compared to the other films tested is not readily discernible. It may, in part, be due to the generally poorer quality of these experimental films.

2.5.3 Use of Tensile Properties as Guidelines for Assessing Requisite Flexibility Characteristics

From table 2 it is seen by comparison of different "forms" of PET or Mylar film, that Mylar-T has greater tensile strength and twist-flex life than Mylar-C at -195°C. The relationship of tensile strength vs. twist-flex life regarding Kapton and Lexan also appears comparable to the above. On the basis of tensile strength alone one would predict Lexan to be superior to Kapton in twist-flex life, which is not the case. Accordingly, when comparing different basic compositions, at least one other parameter is important. In the case of Lexan and Kapton it is seen that the percent elongation values of these films at -195°C are approximately comparable. Accordingly, neither tensile strength elongation nor the combination of the two appear as adequate criteria for twist-flex performance. The twist-flex test involves a number of physical parameters which do not appear capable of simple resolution.

TABLE 6. TENSILE STRENGTH PROPERTIES OF VARIOUS OTHER FIIM MATERIALS

Material	Direction	Temperature	Ultimate Tensile Strength	Yield at .2% Offest	Elongation %	Modulus
PPO (Solvent Cast)	"A"	LN_2	9,000		3.0	
			9,000		2.7	360,000
		Mean	9,000		2.9	360,000
PPO (Solvent Cast	"B"	LN_2	9,000		3.0	330,000
			9,700		3.0	360,000
		Mean	9,350		3.0	345,000
Poly(ethylene isophthalate) (Solvent Cast)	"A"	LN_2	7,700		2.2	356,000
			8,000		1.2	
		Mean	7,850		1.7	356,000
Poly(ethylene isophthalate) (Solvent Cast)	"B"	LN_2	7,200		2.0	418,000
Poly(ethylene isophthalate) (Hat Stretched 4 x 4)		LN_2	9,800		4.0	240,000
			8,400		6.5	116,000
			10,000		6.5	320,000
		Mean	9,400		6.3	225,000

2.6 Coefficient of Thermal Expansion Data for Various Film Materials

In performing the measurement of thermal expansion coefficients a quartz dilatometer was used over the temperature range from -320°F to 2200°F. Figure 40 shows a sketch of this equipment. It can be seen that the sample is rolled into a cylinder one-fourth inch in diameter and two inches long. The exact length of the sample is determined, and it is placed into the quartz tube. A smaller quartz tube, with closed ends, is then set on top of the sample to provide an extension to the dial indicator. The dial indicator is set to zero, and the dilatometer is loaded into the furnace chamber. As the sample expands, the readings on the dial indicator are recorded at each temperature as the differential expansion between the outer quartz tube and the sample. The known expansion of the quartz is then added to the differential expansion at each test temperature to determine the coefficient of expansion.

The coefficient of linear thermal expansion is calculated as follows:

$$\alpha = \frac{\Delta L}{LX(T-T_o)} = \alpha_q T$$

Where:

α = The coefficient of linear thermal expansion of the material under test in either in/in°F or cm/cm°C dpending upon the units used.

ΔL = The differential change in length of the specimen and the quartz outer tube, at the test temperature T in inches.

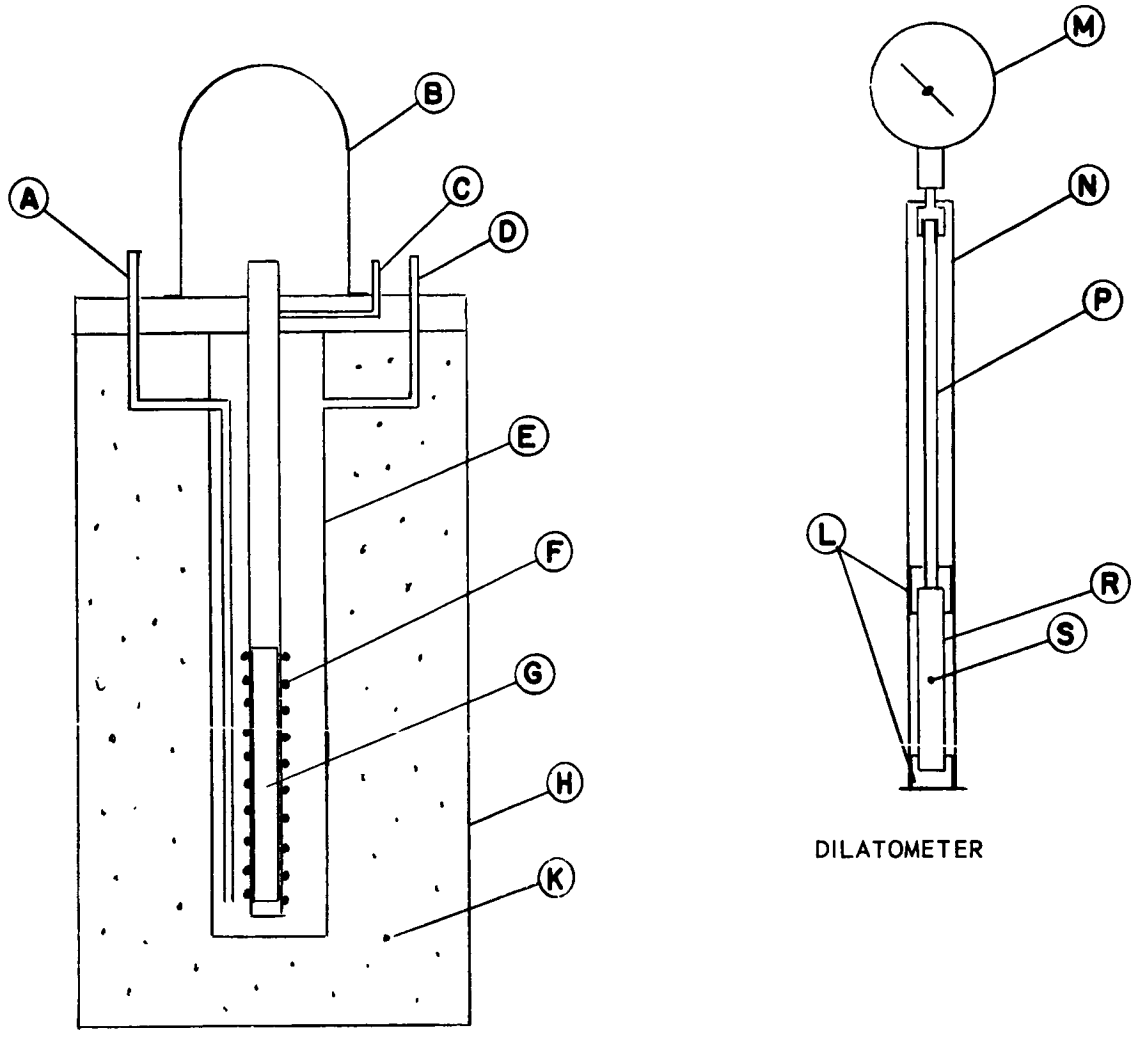
L = The initial length of the test specimen at room temperature (ΔL and L being measured in the same units).

T_o = Ambient temperature.

$\alpha_q T$ = Linear coefficient of thermal expansion of the quartz outer tube at the test temperature T.

2.6.1 Coefficient of Thermal Expansion Data for Various Commercial Films

A number of comparative measurements were made on the commercial Mylar films. This data is presented in table 7, along with NASA data. A sample of Plexiglas was also run for further comparison.



LEGEND

A - LIQUID NITROGEN INLET
B - BELL JAR
C - VACUUM PORT
D - AIR VENT
E - METAL DEWAR
F - HEATER WINDING
G - COPPER CAN
H - METAL HOUSING
K - INSULATION
L - SAMPLE ALIGNER (QUARTZ)
M - DIAL INDICATOR
N - QUARTZ TUBE
P - QUARTZ ROD
R - SPECIMEN
S - THERMOCOUPLE

Figure 40. Dilatometer Assembly.

TABLE 7. COEFFICIENT OF THERMAL EXPANSION DATA FOR MYLAR FILMS*

Material	Direction	Temp.°C	Inches per Inch Expansion (1)	Inches per Inch Expansion (2)
Mylar-T	Longitudinal	-195	5.23×10^{-3}	Mylar 3.6×10^{-3} (Mylar type not identified)
Mylar-T	Transverse	-195	4.24×10^{-4}	
Mylar-C	Longitudinal	-195	4.27×10^{-3}	
Mylar-C	Transverse	-195	4.47×10^{-3}	
Mylar-A	Longitudinal	-195	4.02×10^{-3}	
Mylar-A	Transverse	-195	4.17×10^{-3}	
Plexiglas		-195	9.0×10^{-3}	Plexiglas 9.05×10^{-3}

(1) Melpar data
(2) NASA-Lewis Data

*Differential point values from room temperature to liquid nitrogen temperature.

2.6.2 Coefficient of Thermal Expansion Data for Experimental Films

The following experimental films were analyzed for coefficient of thermal expansion properties and are listed in table 8; (a) a series of sequentially biaxially oriented poly(ethylene terephthalate) films prepared on a T. M. Long Co. "Film Stretcher" by the Tennessee Eastman Chemical Company; (b) a series of simultaneously biaxially oriented poly(ethylene terephthalate) films prepared on the "hat stretcher" by DeBell and Richardson Company; (c) poly (2,6-dimethyl phenylene oxide) (PPO) solvent cast films; (d) specimens of poly(ethylene isophthalate) films, solvent cast and hat stretched.

The following observations were made:

(a) The twist-flex testing of a film at liquid nitrogen temperature increases the coefficient of thermal expansion value of that film considerably.

TABLE 8. COEFFICIENT OF THERMAL EXPANSION DATA FOR VARIOUS EXPERIMENTAL FILMS (ALL EXPERIMENTS CARRIED OUT IN DUPLICATE)

Material (sequentially biaxially oriented PET films)	Direction	Inch/Inch Expansion
TE-F #1 (Heat Set)	--	2.6×10^{-3}
TE-F #2 (Heat Set)	--	3.0×10^{-3}
TE-F #3 (Not Heat Set	--	1.5×10^{-3}
TE-G-1 (Not Heat Set) (before twist-flexing)		7.2×10^{-4}
TE-G-1 (Not Heat Set) (after twist-flexing)		1.8×10^{-3}
TE-G-1 (Not Heat Set)	"A"	6.0×10^{-4}
TE-G-1 (Not Heat Set)	"B"	6.4×10^{-3}
TE-K-1 (Heat Set)	--	3.2×10^{-3}
TE-L-1 (Heat Set)	"A"	4.7×10^{-3}
TE-L-1 (Heat Set)	"B"	9.1×10^{-3}
TE-L-1 (Not Heat Set)	--	7.0×10^{-3}
Simultaneously Biaxially Oriented PET Films		
DR-6X-112°C, Heat Set, 10 sec, 200°C		2.7×10^{-3}
DR-4X-91°C, Heat Set, 10 sec, 200°C		2.4×10^{-3}
DR-4X-101°C, Heat Set, 10 sec, 200°C		2.4×10^{-3}
DR-4X-101°C, Heat Set, 30 sec, 200°C		2.4×10^{-3}
DR-4X-101°C, Not heat set,		3.6×10^{-3}

TABLE 8 (Continued)

Other Films (DR)

PPO Solvent Cast Film	1.1×10^{-2}
Poly (ethylene isophthalate) solvent cast film	1.4×10^{-2}
Poly (ethylene isophthalate) hat stretched-4X, not heat set	9.7×10^{-3}

Code:

Identification of PET Films (Sequentially Biaxially Oriented)

TE = Tennessee Eastman

F #1 = 4 x 4 stretch ratio, 170-175°F stretch temperature, 0.5 inches/minute stretch rate
Heat set 10 sec. at 200°C

F #2 = Same as F-1

F #3 = Same as F-1 except: not heat set.

G-1 = 4 x 4 stretch ratio, 198-204°F stretch temperature,

G-1 (After twist-flexing) = 4" x 11" film sample was twist-flexed in liquid nitrogen for 220 cycles and then analyzed for its thermal expansion coefficient

K-1 = 3 x 3 stretch ratio, 200°F stretch temperature, 8.0 inches/min. stretch rate.

L-1 = 3.5 x 3.5 stretch ratio, 200°F stretch temperature, 8.0 inches/min stretch rate

Simultaneously Biaxially Oriented PET Films

DR = DeBell and Richardson
Other designations as shown in table

Other Films

Designations as shown in table.

Thus, for a film that had been stretched 4 x 4 at 198°F - 204°F and at a stretch rate of 8.0 inches/min. and not heat set, the representative values were 7.2×10^{-4} before twist-flexing and 1.8×10^{-3} after twist-flexing.

(b) The simultaneously biaxially oriented PET samples all have coefficients of thermal expansion values in the range of Mylar C.

(c) The PPO and poly(ethylene isophthalate) films, each solvent cast, had the greatest expansion values (in the range of 10^{-2} inches/inch).

(d) The coefficient of thermal expansion values for the two directions of the Tennessee Eastman G-1 film were very close to those of the two directions in Mylar T. This is surprising since the films prepared by Tennessee-Eastman were presumed to possess balanced orientation. The values of interest were:

A direction, G-1, 6.0×10^{-4}; Mylar T, transverse, 4.24×10^{-4};

B-direction, G-1, 6.4×10^{-3}; Mylar T, longitudinal, 5.23×10^{-3}.

In conclusion, the biaxial orientation parameters studied appear to have an influence on the coefficient of thermal expansion properties of these films. However, no obvious trends are discernible in attempting to relate changes in biaxial orientation parameters to the resultant coefficient of thermal expansion values of the films.

2.7 Permeability Data for Various Film Materials

2.7.1 Permeability Apparatus and Procedures

A schematic diagram of the apparatus used in determining permeability data is shown in figure 41.

The test chamber was constructed of 304 S.S. and contained a groove for a Teflon O-ring. Three vacuum valves were included in the system for closing off sections during test runs.

The test specimen having an exposed cross sectional area of 5.06 sq.cm. (cleaned with alcohol) was inserted into the test chamber. The test chamber was bolted shut and evenly torqued with seven pounds to insure a vacuum tight seal. With valve "B" closed and valve "A" open, the gate valve was opened to the vacuum system. The system is evacuated to 5×10^{-6} torr.

With the system in this state of operation, the gate valve is closed and the leak rate of the system is established over a 30 minute run. At that time valve "A" is closed and valve "B" is opened to admit one psi of gas behind the membrane.

The gas diffusion is then taken for 30 minutes and valve "A" is opened; the gate valve is opened to evacuate the system again for the next test run.

Room temperature measurements were taken first, consisting of testing for the diffusion of hydrogen and nitrogen gas through the sample. The test chamber was then immersed in liquid nitrogen and after sufficient time to cool the sample, the same test runs were taken again. Hydrogen gas was tested first, at room temperature and liquid nitrogen temperature to see if any gas was diffusing. If the diffusion rate was very small, or none, the nitrogen gas runs were deleted from the test.

The calculations used in arriving at the permeability data were as follows:

H_2 and N_2 at reduced pressures ($<10^{-3}$) behave much like ideal gases and in the following calculations are considered as such. In the diffusion system under consideration, there are three basic sources of pressure and accordingly all partial pressures follow the gas law:

$$PV = nRT$$

The three sources of partial pressure are

Pr = residual gas in the system

Pl = gas leakage in the system and partial pressure of adsorbed impurities

Px = partial pressure of gas diffused through the sample

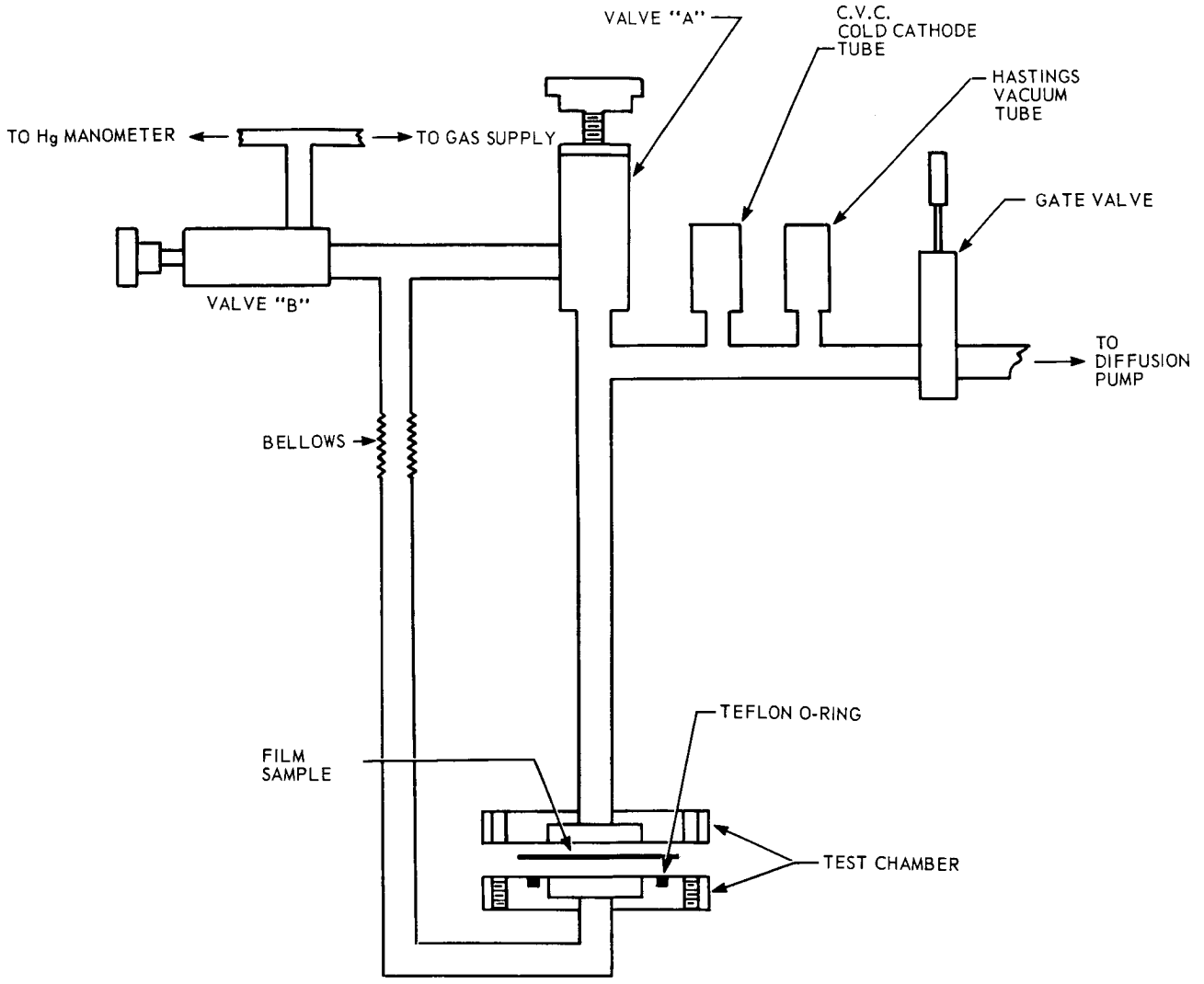


Figure 41. Permeability Apparatus

For the constant volume system,

$$\frac{Px\ V_s}{T_S} = \frac{Pstp\ V_X}{Tst} = K$$

Where V_S is the volume of the system; T_S, the Kelvin temperature of the system; Pstp = one atmosphere, and T_{st} is standard temperature. Thus, V_X will give the equivalent volume of the diffused gas.

The time-rate curve for Pr + Pe + Px is obtained, and from this is subtracted the time-rate curve for $P_r + P_1$ (baseline curve). From the resulting value of P_x over time, the volume of the diffused gas at STP can be calculated from

$$V = \frac{(V_s)\ (P_x)\ (1.316 \times 10^{-6})}{(t)\ (A)\ (T)}$$

Where P_x is in microns, t is thickness of sample in cm, A is area in cm^2 and T is time.

The resulting number will represent volume (in ml) of diffused gas per cm of thickness per cm^2 of area per 24 hours.

2.7.2 Permeability Data For Various Polymeric Films

The permeability data for various polymeric films are shown in table 9.

The test results disclosed that commercially available films, as well as experimental films, are not homogeneous. As far as permeability to nitrogen and hydrogen at room temperature is concerned, the films are either not permeable or quite permeable depending on the particular portion of film tested. It can be seen that polymer films of the thickness tested are permeable; however the sensitivity of the test method appears to be too low to determine these values with accuracy.

TABLE 9. PERMEABILITY DATA FOR VARIOUS 1/2 MIL POLYMERIC FILMS

(Units of permeability are in Volume (ml at STP) per cm of thickness per cm^2 of area per 24 hours = V/ cm/ cm^2/ 24 hours)

Material	Sample	Room Temperature N_2	Room Temperature H_2	Liquid Nitrogen Temp. N_2	Liquid Nitrogen Temp. H_2
Mylar T	1	0	5.41	--	4.1×10^{-2}
	2	-	0.68	--	--
	3	-	33.5	--	--
Mylar C	1	307	810	--	3.6×10^{-2}
	2	--	0.72	--	--
	3	--	15.3	--	--
TE-E-1 (Heat Set)	1	--	40.2	--	--
TE-E (Not Heat Set)	1	--	44.7	--	--
TE-F (Heat Set)	1	17.6	1260.	0	0
TE-F (Not Heat Set)	1	3.6	33	--	3.6×10^{-2}
DR-A (Heat Set)	1	--	2.4	--	--
DR-B (Heat Set)	1	--	0	--	0
	2	--	8.2	--	--
DR-C (Not Heat Set)	1	1.8	26.6	2.3×10^{-2}	13.5×10^{-2}
	2	--	13.	--	--
DR-D (Heat Set)	1	--	13	--	0
	2	(Failed after 1-3/4 min.)			

TABLE 9(CONTINUED). PERMEABILITY DATA FOR VARIOUS POLYMERIC FILMS

Specimen	Stretch Temperature	Stretch Ratio	Stretch Rate	Heat Set
TE-E-1 (Heat Set)	168-172°F	3.5 x 3.5	8.0	10 Sec/200°C
TE-E (Not Heat Set)	168-172°F	3.5 x 3.5	0.5	---
TE-F (Heat Set)	170-175°F	4 x 4	0.5	10 Sec/200°C
DR-A (Heat Set)	101°C	4 x 4	-	10 Sec/200°C
DR-B (Heat Set)	91°C	4 x 4	-	10 Sec/200°C
DR-C (Not Heat Set)	101°C	4 x 4	-	---
DR-D (Heat Set)	112°C	6 x 6	-	10 Sec/200°C

CODE: TE = Tennessee Eastman Prepared Specimens

DR = DeBell and Richardson Prepared Specimens

2.8 Metal Catalyst Residues in Several Commercial Polyesters

Metal catalyst residues in several commercial polyesters were measured by emission spectroscopy in order to more completely identify subtle differences in composition which might contribute to flexibility at cryogenic temperatures. This data is shown in table 10. In table 11 the metal catalyst residues are grouped according to families in the Periodic Table.

It can be seen that Mylar C and Mylar T do not contain the same major residues, although the total amount of metals present is approximately the same. Mylar A is relatively low in residue content and Vitel VMF-414 is intermediate. Mylar C contains Na, Ca, Al, Si, Sb, Cu, Fe, and Zn in about the same amounts while Mylar T contains Ca and Al as the major metal residues. Another major difference is that Mylar C contains Zn while Mylar T does not.

A compilation of available data on the above indicated series of polyester films is presented in table 12. Values included are metal catalyst residues, values, and density.

2.9 The Utility of Broad-Line NMR as a Diagnostic Screening Tool for Evaluating Polymers for Cryogenic Applications

At the start of this program in May 1964 it was believed that broad-line NMR might have utility as a diagnostic screening tool for the evaluation or ranking of polymers in the bulk or unfabricated form. If this were true then a great deal of time and money could be saved in eliminating the steps required for conversion of a raw polymer into an oriented thin film. Various commercial and experimental polymers in bulk form and in final film form were subjected to NMR studies at Harvard University under the direction of Prof. Rochow. Work was started and continued over the period from about 15 July 1964 to 30 March 1965.

In mid-March Dr. T. Serafini of NASA-Lewis Research Center requested that the opinion of Dr. Wm. Slichter of Bell Telephone Laboratories be solicited concerning the theoretical validity of using broad-line NMR for evaluating the potential flexibility of polymers for cryogenic applications. A summary of some of the key points made by Dr. Slichter is included in the Appendix of this report under the "Meetings with Consultants" section.

The data generated by the investigation of the various polymers utilizing NMR is included in tables 13 through 21 together with some possible interpretations of these results.

Included in Appendix B is a detailed description of the apparatus used for this program.

TABLE 10 - CATALYST RESIDUES IN MYLAR FILM, TYPES A, C, AND T AND VITEL VMF-414 RESIN

(By Emission Spectroscopy)

Metal	Mylar A	Mylar T	Mylar C	Vitel VMF-414
Aluminum	>4.5	30*	>12.5	3
Antimony	<0.04	6	12.5	<1
Arsenic	<0.04	0.3	<0.1	-
Barium	<0.004	-	0.1	-
Beryllium	<0.004	-	0.01	-
Bismuth	<0.004	7	<0.01	-
Boron	0.05	0.1	0.5	<1
Cadmium	<0.45	3	5.0	<2
Calcium	0.23	30*	12.5	<2
Chromium	0.18	0.6	1.0	<0.2
Cobalt	0.23	3	1.0	-
Copper	0.31	0.3	10.0	<2
Gallium	<0.004	-	<0.01	-
Germanium	<0.004	-	-	-
Indium	<0.004	-	<0.01	-
Iron	4.5	3	>12.5	10
Lead	<0.04	-	0.7	-
Magnesium	0.23	9	3.0	>1
Manganese	0.05	0.3	0.7	-
Molybdenum	<0.004	7.1	0.05	<1
Nickel	0.23	0.6	1.0	<2
Sodium	-	6	>12.5	>10
Silicon	0.23	6	>12.5	>10
Silver	<0.004	3	1.0	-
Tin	0.02	0.6	3.0	-
Titanium	1.8	3	1.0	<16
Tungsten	<0.04	-	<0.1	-
Vanadium	<0.004	0.1	0.03	>1
Zinc	<0.05	-	>>12.5	>10
Zirconium	>0.05	7.1	<0.05	-

< = less than
> = greater than
Values in parts per million on sample basis.

*Al, Ca, Major Metals Zn absent for Type T

TABLE 11. - SUMMARY OF METAL ATOM IMPURITIES IN MYLAR A, C, T, FILMS AND VITEL VMF-414 RESIN

	Mylar A	Mylar T	Mylar C	Vitel VMF-414
Total Metal Impurities (in ppm)	15	130	125	75
Group IA metals	0	Na(6)	Na(13)	Na(11)
IIA metals	0	Ca(30)	Ca(12.5)	0
IIIA metals	Al(5)	Al(30)	Al(13)	Al(3)
IVA metals	0	Si(6)	Si(13)	Si(11)
VA metals	0	Sb(6), Bi(7)	Sb(12.5)	0
Transition metals	Fe(4.5) Ti(1.8)	Mo(7) Ti(3) Zn(7)	Cu(10) Fe(13) Zn(15)	Ti(15) Zn(11)

TABLE 12. - VARIOUS PROPERTIES OF MYLAR A, C, T, AND VITEL VMF-414 RESIN

Property	Mylar A	Mylar T	Mylar C	Vitel VMF-414
Metal Impurities (in ppm)	15	130	125	75
"Significant" Metals	Al,Fe,Ti	Al,Ca,Sb Bi,Mo,Zr	Al,Ca,Sb Fe,Zn	Al,Ti,Zn
(η_{inh})	0.56	0.56	0.54	0.67
Density	1.384	1.385	1.400	--

TABLE 13. BROAD-LINE NMR RESULTS FOR SEVERAL EXPERIMENTAL POLYMERS AND KAPTON

Sample	25°C			-85°C			-195°C		
	A	B	C	A	B	C	A	B	C
Poly(1,4-phenylene terephthalate)	5.48	.17	1.7	6.07	.10	1.9	6.08	.07	1.9
Poly(1,4-phenylene isophthalate)	6.00	.4	1.7	6.40	.20	1.7	6.84	.12	1.9
Poly(ethylene terephthalate) (73% crystalline)	7.62	.23	1.9	8.40	.10	1.9	8.67	.20	2.1
Poly(ethylene terephthalate) (unoriented, amorphous) (0-3% crystalline	5.03	.20	1.7	6.25	.20	1.7	6.55	.10	1.9
Poly(ethylene terephthalate) hat-stretched, not heat set (15-20% crystalline)	5.19	.15	1.7	6.90	.20	1.7	7.50	.12	1.9
Kapton	3.88	.10	1.0	5.10	.10	1.3	4.95	.16	1.3
Poly(1,2-propylene terephthalate)	4.79	.12	1.5	5.55	.10	1.5	7.32	.25	1.7
Poly(1,4-phenylene bis(dimethyl siloxane))	0.5	--	--	4.71	.05	1.3	5.42	.05	1.3

A: Line width

B: Deviation all in gauss units

C: Modulation

TABLE 14. BROAD-LINE NMR DATA FOR A SERIES OF POLYESTERS AT 25°C

Sample	Line Width (Gauss Units)	Deviation (Gauss Units)	Modulation (Gauss)
Mylar Type A Film	5.95	0.06	1.6-1.8
Poly(ethylene isophthalate)	4.76	0.21	1.6-1.8
Poly(ethylene terephthalate)	7.04	0.09	1.6-1.8,2.6
Poly(trimethylene terephthalate)	5.92	0.08	1.6-1.8,2.6
Poly(tetramethylene terephthalate)	6.83	0.12	1.6-1.8,2.6
Poly(pentamethylene terephthalate)	5.58	0.08	1.6-1.8
Poly(hexamethylene terephthalate)	5.04	0.10	1.6-1.8
Poly(diethyleneoxy terephthalate)	5.10	0.09	1.6-1.8
Poly(dimethylene cyclohexylene terephthalate) Type 0 Resin	4.63	0.09	1.7
Poly(dimethylene cyclohexylene terephthalate) Type 0 Powder*	4.65	0.16	1.6-1.8
Poly(dimethylene cyclohexylene terephthalate) Type 2 Resin	5.72	0.11	1.7
Poly(dimethylene cyclohexylene terephthalate) Type 2 Powder*	5.61	0.13	1.7
Kodar Film	5.70	0.08	1.7
Vitel VMF-414 Resin	4.42	0.10	1.9
Vitel VMF-414 Powder*	5.16	0.11	1.9
Mylar Type C Film	6.20	0.15	1.7
Amorphous Mylar Type A Sheet (unoriented)	5.04	0.16	1.7

*Powder produced from resin by grinding

TABLE 15. NMR DATA FOR A SERIES OF POLYESTERS AT -85°C ±3%

Sample	Line Width (Gauss Units)	Deviation (Gauss Units)	Modulation (Gauss)
Mylar Type A Film	7.45	0.06	2.2
Poly(ethylene isophthalate)	6.23	0.42	2.2
Poly(ethylene terephthalate)	8.12	0.17	2.2
Poly(trimethylene terephthalate)	7.42	0.09	2.2
Poly(tetramethylene terephthalate)	7.90	0.08	2.2
Poly(pentamethylene terephthalate)	7.36	0.15	2.2
Poly(hexamethylene terephthalate)	8.31	0.19	2.2
Poly(diethyleneoxy terephthalate)	6.68	0.18	2.2
Poly(dimethylene cyclohexylene terephthalate), Type 0 Resin	ca:9	0.40	1.9
Poly(dimethylene cyclohexylene terephthalate), Type 0 Powder*	8.78	0.30	2.2
Poly(dimethylene cyclohexylene terephthalate), Type 2 Resin	>9.5	--	1.9
Poly(dimethylene cyclohexylene terephthalate), Type 2 Powder*	>9.5	--	1.9
Kodar Film	>9.5	--	1.9
Vitel VMF-414 Resin	6.25	0.10	1.9
Vitel VMF-414 Powder*	7.12	0.05	1.9
Mylar Type C Film	7.92	0.10	1.9
Amorphous Mylar Type A (unoriented)	6.37	0.06	1.9

*Powder produced from resin by grinding.

TABLE 16. NMR DATA FOR A SERIES OF POLYESTERS AT -195°C ± 3°C

Sample	Line Width (Gauss Units)	Deviation (Gauss Units)	Modulation (Gauss)
Mylar A Film	7.95	0.05	2.6
Poly(ethylene isophthalate)	7.24	0.04	2.6
Poly(ethylene terephthalate)	8.70	0.13	2.6
Poly(trimethylene terephthalate)	8.78	0.20	2.6
Poly(tetramethylene terephthalate)	9.28	0.30	2.6
Poly(pentamethylene terephthalate)	ca.9.00	--	2.6
Poly(diethyleneoxy terephthalate)	7.03	0.02	2.6
Poly(dimethylene cyclohexylene terephthalate) Type 0 Resin	≥15	--	--
Poly(dimethylene cyclohexylene terephthalate) Type 0 Powder*	≥15	--	--
Poly(dimethylene cyclohexylene terphthalate) Type 2 Resin	≥15	--	--
Poly(dimethylene cyclohexylene terephthalate) Type 2 Powder*	≥15	--	--
Kodar Film	ca.14	--	2.2
Vitel VMF-414 Resin	6.52	0.10	2.2
Vitel VMF-414 Powder*	7.25	0.15	2.2
Mylar Type C Film	7.95	0.12	2.2
Amorphous Mylar Type A Sheet (unoriented)	6.50	0.16	2.2

* Powder produced from resin by grinding.

TABLE 17. NMR DATA FOR VARIOUS POLYMERS AT 25°C

Polymer	Line Width (Gauss Units)	Deviation (Gauss Units)	Modulation (Gauss)
Mylar Type T. Film	6.35	0.10	1.7
Vitel VFR 338 Film	5.38	0.13	1.7
Vitel VMF-414 Film	6.16	0.08	1.7
Vitel VMF-414 Amorphous Sheet	4.88	0.11	1.7
Lexan Film	4.26	0.10	1.3
Poly(2.6-dimethyl phenylene oxide)(PPO) Powder	4.17	0.15	1.3
Poly(hexafluoropentamethylene terephthalate) Powder			
Proton Resonance	4.58	0.10	1.7
Fluorine Resonance	3.76	0.30	1.7

TABLE 18. NMR DATA FOR VARIOUS POLYMERS AT -85°C

Temperature -85° ±3°C	Line Width (Gauss Units)	Deviation (Gauss Units)	Modulation (Gauss)
Mylar Type T Film	7.64	0.11	1.9
Vitel VFR-338 Film	7.63	0.08	1.7
Vitel VMF-414 Film	7.63	0.12	1.9
Vitel VMF-414 Amorphous Sheet	6.33	0.10	1.7
Lexan Film	6.02	0.15	1.5
Poly(2.6-dimethyl phenylene oxide)(PPO) Powder	4.83	0.09	1.5
Poly(hexafluoropentamethylene terephthalate) Powder			
Proton Resonance	6.53	0.13	1.7
Fluorine Resonance	6.40	0.30	1.7

TABLE 19. NMR DATA FOR VARIOUS POLYMERS AT -195°C ± 3°C

Polymer	Line Width (Gauss Units)	Deviation (Gauss Units)	Modulation (Gauss)
Mylar Type T Film	7.65	0.11	2.2
Vitel VFR-338 Film	8.00	0.13	2.2
Vitel VMF-414 Film	8.02	0.12	2.2
Vitel VMF-414 Amorphous Sheet	6.35	0.15	1.9
Lexan Film	5.90	0.06	1.7
Poly(2.6-dimethyl phenylene oxide)(PPO) Powder	5.37	0.14	1.7
Poly(hexafluoropentamethylene terephthalate) Powder			
Proton Resonance	7.26	0.30	1.7
Fluorine Resonance	7.16	0.30	1.7

TABLE 20.. NMR DATA FOR A SERIES OF SILICONE POLYMERS

at -195°C

Polymers	Line Width (Gauss)	Modulation (Gauss)
Methyl Silicone	5.05	1.3
Ethyl Silicone	6.48	1.9
Methyl Phenyl Silicone	7.72	1.7
Chlorophenul Silicone	5.07	1.7
Amyl Silicate	13.0	2.2
Bouncing Putty	4.60	0.8
Minne Polymer I	5.51	0.8
SE 472 U	4.79	1.1
No. 81083 Silicone Grease	4.57	0.6
Neoprene Rubber (for comparison)	8.80	1.9

References For Silicone Polymers

The following references (in page numbers) refer to: "An Introduction to the Chemistry of the Silicones" by E. G. Rochow, John Wiley and Sons, New York, Second Edition, 1946 and 1951 and references therein.

Methyl Silicone	Pages 94-97
Ethyl Silicone	Pages 97-98
Methyl Phenyl Silicone	Page 105
Chlorophenyl Silicone	Page 103
Bouncing Putty	Page 97
Amyl Silicate	Page 98

References to Minne Polymer I can be found in: Rochow, E. G. and Minne, R. N., J A C S, 82, 5625 (1960) and in: Kummer, D. ONR Technical Report Contract No. Nonr-1866(13) December, 1962 and January 1963 Chemistry Branch, Office of Naval Research.

TABLE 21. NMR LINE WIDTH - TEMPERATURE PROFILE POLY(1,4-PHENYLENE BIS(DIMETHYLSILOXANE))

Temperature (^{o}C)	Line Width (Gauss)	Second Moment (Gauss^{2})
25	< 0.5	< 1.0
+15	2.8 ± 0.1	3.1 ± 0.1
0	4.1 ± 0.1	3.8 ± 0.3
-90	5.0 ± 0.2	5.4 ± 0.6
-196	5.5 ± 0.2	6.9 ± 0.3

(There is a sharp transistion point in line width and second moment at approximately +15^{o}C.)

Interpretation of Broad Line NMR Data

Dr. Slichter has suggested that broad-line NMR is measuring the following.

1. The line widths at -195°C are a measure of the proton packing in the rigid lattice. The proton packing, in turn, is seen to be dependent upon the proton density of the basic polymer composition, crystallinity, the particular crystalline form of the polymer, and residual motions of specific groups, such as pendant methyl groups.

2. The change of line width with temperature below Tg measures how fast the polymer structure becomes rigid on decreasing temperature. This in turn depends upon the type of motion being frozen out; the approximate order being: lattice vibrations (at highest relative temperature), chain deformation (next), specific group rotations (last or at the lowest temperature). Below Tg we are presumably looking only at the latter in conjunction with the effect of proton "composition" as discussed under (1) above.

Variation of Line Widths with Different Crystallinity Levels for Poly (ethylene terephthalate.)

These data are shown in figure 42 and 43. It is seen that the line widths at -195°C parallel the calculated crystallinity levels based on densities. Indeed the relationship appears to be approximately linear between 20-70% crystallinity, though this is very likely fortuitous (see figure 44).

Commercial PET Films

The line width of Mylar-T at -195°C is slightly less than that of Mylar-C (beyond experimental error). This agrees with the fact that the Mylar-T has a lower density than Mylar-C (1.385 vs. 1.400). Mylar-A and Mylar-T, on the other hand, have different line widths at -195°C and yet have the same density (at 25°C). Analogously, Mylar-A and Mylar-C, though possessing identical line widths at -195°C have significantly different densities (at 25°C); Mylar-A having a density of 1.384. It is also interesting to note that Mylar-A shows the greatest change in line width from -85°C to -195°C. Mylar-C and Mylar-T, on the other hand, appear to have reached their maximum rigidity at temperatures above -85°C. Finally it is of interest to note that the line width-crystallinity points for Mylar-C and Mylar-T do not fall on the same line as those for the samples obtained from Mylar-A.

Vitel VFR-338 and Vitel VMF-414 films appear identical on the basis of line widths at -85°C and -195°C and resemble Mylar-A in their change in line widths with temperature and their line width values at -195°C. The change in their line widths with temperature over the range of -85° to -195°C does however appear to be somewhat less than that of Mylar-A.

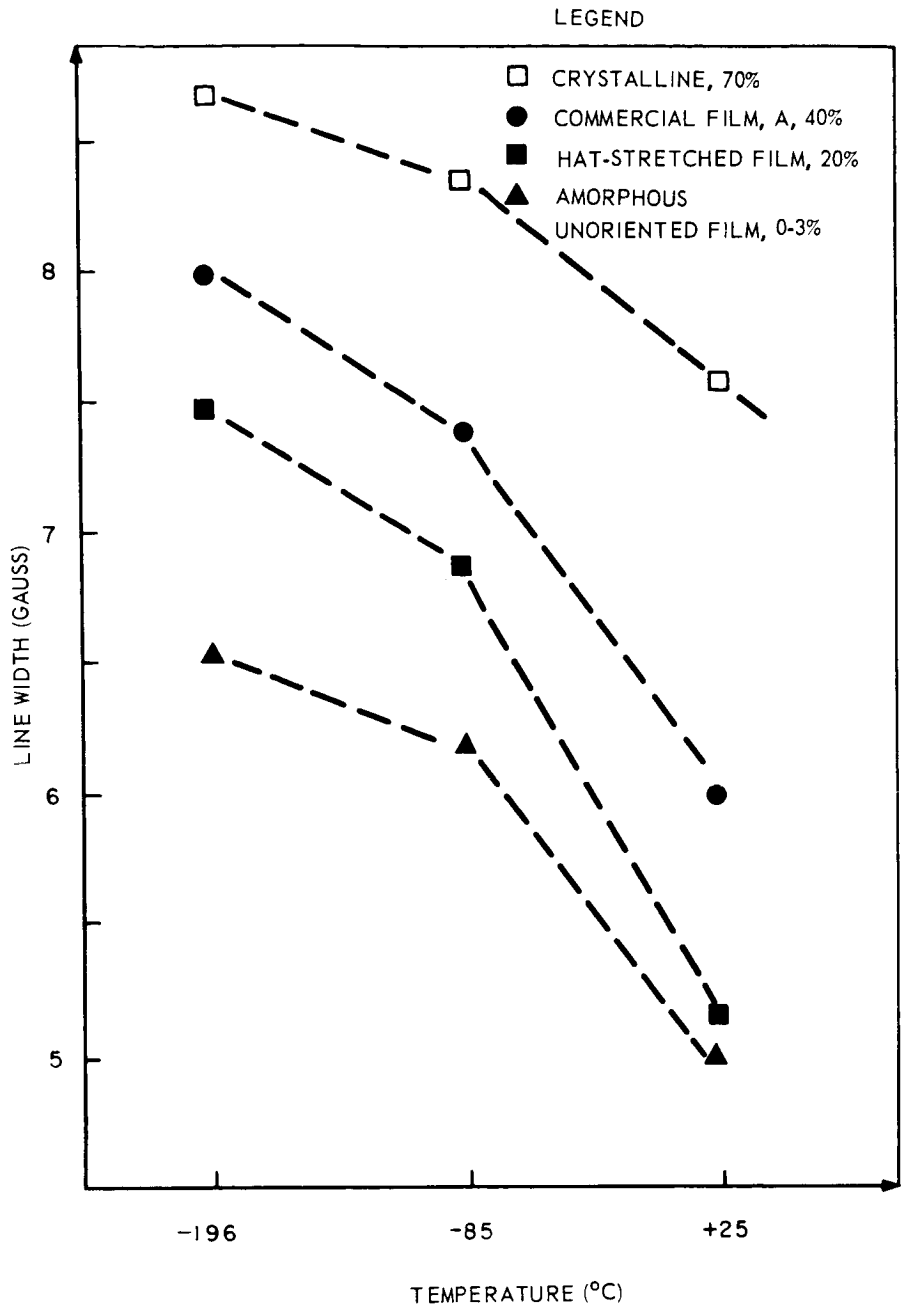


Figure 42. NMR Line Width Values for Poly(ethylene terephthalate) at Several Levels of Crystallinity at Different Temperatures

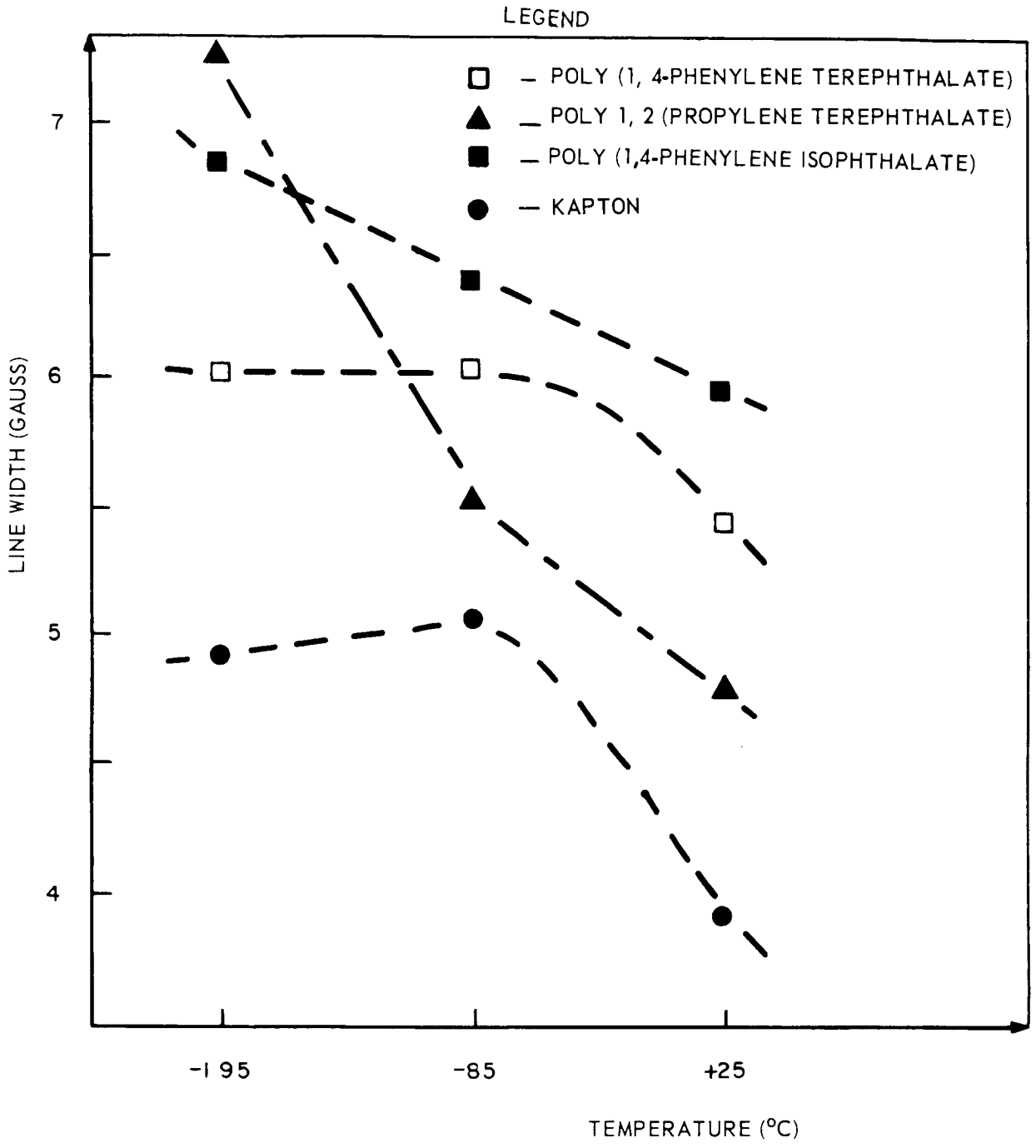


Figure 43. NMR Line Width Values for Several Polymers at Different Temperatures

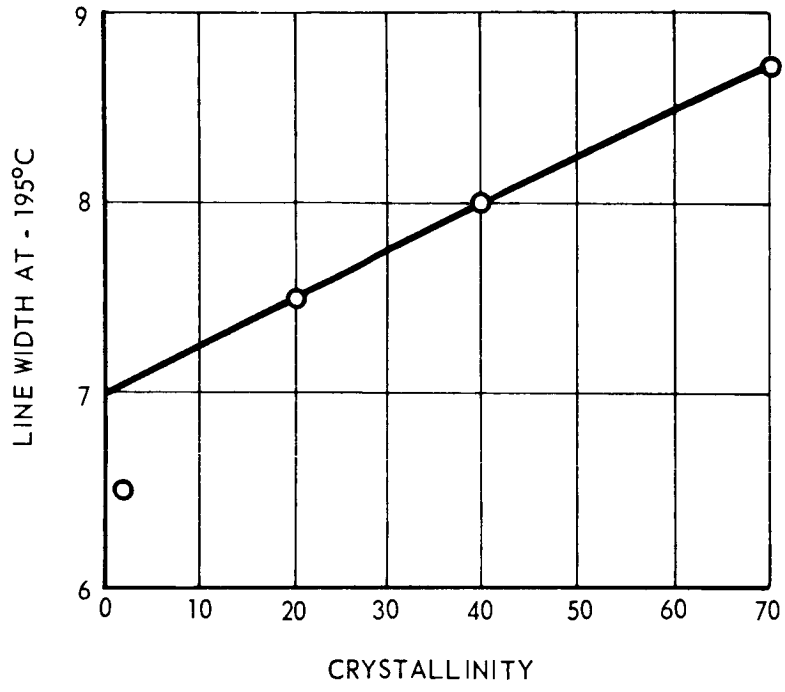


Figure 44. Variations of Line Width at -195°C vs. Level of Crystallinity for Polyethylene Terephthalate (Mylar A).

These results can be interpreted on the basis that,

(1) Mylar-A contracts more on cooling to -195°C than either Mylar-C or T and has a greater density, more comparable to Mylar-C, at -195°C than at 25°C. This may suggest that the amorphous region in Mylar-A has a greater amount of the gauche form of PET, which on cooling contracts more than the amorphous region in Mylar-C;

(2) Mylar-C and T have about the same processing history except for the additional stretch given to Mylar-T. Mylar-A, on the other hand, differs significantly from Mylar-C and T in either processing (e.g., spherulite size formation), stretching conditions, or it might even contain some isophthalate copolymer. Vitel VFR-338 and Vitel VMF-414 appear to be identical and differ in composition from Mylar C and T in concurrence with the report that the former contain some isophthalate copolymer.

Poly (Ethylene Terephthalate)(PET) vs. Poly (Ethylene Isophthalate)(PEI)

Each polymer contains the same number of protons. Hence, on the basis of proton packing density alone the line widths for the rigid lattices should be identical. Experimentally, the line width of PET is considerably greater than that of PEI at -195°C. A possible interpretation for this fact is that PET is either more crystalline than PEI, or that the former's crystalline structure is tighter (which would favor greater crystallinity). In theory, each polymer is capable of forming a planar conformation. In practice, on the other hand, PEI may contain a greater proportion of twisted benzene rings, and hence its "packing" may be looser than that of PET. This is of course quite speculative.

Inspection of the change of line width with temperature in the region of -85 to -195°C shows that PEI has a longer way to go to achieve its maximum rigidity than does PET. Again this may reflect the lower crystallinity of PEI.

The Series C_2, C_3, C_4, C_5, and C_6 - Poly(Methylene Terephthalates)

The absolute line widths at -195°C parallel the total number of protons present per monomer unit with the following exception. The C_4 terephthalate has a significantly greater line width than the C_6 terephthalate even though the latter has a greater number of protons per monomer unit. This discrepancy may be due to the greater crystallinity of the C_4 terephthalate though this has not been determined. Moreover it is probable that the poly (methylene terephthalates) here studied were all of different crystallinities. The observed line widths may reflect more the proton packing within each molecule rather than between near neighbors. Information is required on the actual crystallinities (based on X-ray measurements of the dimensions of the unit cell) before one can unambiguously interpret the NMR results.

Upon inspecting the slopes of the lines for the line widths at -85°C and -195°C it is evident that the C_8 terephthalate has the greater slope. In other words, it appears from this data alone that the C_8 terephthalate has a longer way to go to achieve its maximum state of rigidity than the other poly methylene terephthalates studied. Unfortunately, this polymer does not lend itself to biaxial orientation by conventional methods because of its low Tg.

3. CONCLUSIONS

3.1 The Twist-Flex Method for Determining Comparative Flexibility Properties of Films

In studying the twist-flex method, particularly at -195°C, several key observations were made. These include the following: (1) A comparison testing program conducted by Melpar in collaboration with NASA-Lewis demonstrated that the two twist-flex machines yield similar results using a standardized test procedure. (2) The size of the film specimen used for twist-flex testing has a very significant effect on the twist-flex life of that film. (The smaller the sample size the greater the twist-flex life of the film). Furthermore, the 4 in. x 11 in. film size in general yields results that are difficult to use in determining a "cycles to failure" value for a particular film. This is due to a fairly large number of early failures observed during a series of tests on a particular film material. These early failures are not nearly so pronounced when the 4 in. x 4 in. film size is used, probably because a smaller stress is applied when the 4 in. x 4 in. is twist-flexed as compared to the 4 in. x 11 in.

3.2 The Effect of Biaxial Orientation Parameters on the Twist-Flex Life of PET Films

The conditions used during sequential biaxial orientation of PET films have a pronounced effect on the twist-flex life of these films at liquid nitrogen temperature. In particular the stretch ratio as well as the stretch temperature appear to be important factors in determining the twist-flex life of PET films at this temperature. Films stretched 3.5 x 3.5 or 4 x 4 at about 170°F have greater resistance to twist-flexing than does a film stretched 3.5 x 3.5 at about 200°F. In addition, films stretched at about 170°F at a stretch ratio of 3.5 x 3.5 or 4 x 4 have greater twist-flex resistance than do films stretched 2 x 2 at this temperature.

The rate of stretch during biaxial orientation, either 0.5 inches per minute or 8.0 inches per minute, has no effect on the twist-flex life of the resultant films, although higher rates of stretch may be significant.

Heat-setting PET films at 200°C for 10 seconds has no apparent effect on their twist-flex endurance, under the conditions of test in this program. It should be noted however that amorphous unoriented Mylar sheet does tend to crystallize on long standing[12] and that there is a possibility that stretched but not heat-set films may also tend to crystallize on long standing.

3.2.1 Twist-Flex Life of Experimental PET Films Compared to Mylar-C and T.

The twist-flex life of PET film prepared by stretching 4 x 4 at about 170°F at a stretch rate of 0.5 inches per minute is greater than that of

Mylar-C. For this film no failure is observed up to 1000 cycles, where Mylar-C fails at about 700 cycles employing 4 in. x 2 3/4 in., 1/2 mil films at liquid nitrogen temperature. This film may be as good as Mylar-T which was found to withstand 2000 cycles without failure. However, not enough material was available to establish this.

3.3 Superior Resistance of Mylar-T to Twist-Flexing

Mylar-T is superior to Mylar-C and all other polymer films examined to date in twist-flex life to failure at -195°C. In particular the twist-flex life of Mylar-T is greater than 350 cycles to failure while that of Mylar-C is about 75 cycles to failure (employing 4 in. x 4 in., 1/2-Mil films).

Samples of 1/2-Mil Mylar T film, 4 in. x 2 3/4 in. in size withstood 2000 cycles without failure where Mylar-C failed at about 700 cycles.

3.4 Poly(Ethylene Isophthalate) Films

Poly(ethylene isophthalate) can be formed into amorphous film which can be biaxially stretched 4 x 4 to yield thin films of promising value.

3.5 PPO Polymer Films

Poly (2,6 -dimethyl phenylene oxide) (PPO) can be solvent cast from chloroform solution to yield 0.7 to 1.5 mil films. These films show fair twist-flex performance at -195°C, considering the thickness of the film used.

3.6 Utility of Broad-Line NMR as a Diagnostic Screening Tool

From the results of this program it was concluded that broad-line NMR is of no value for assessing the "flexibility" of a polymer at cryogenic temperatures.

4. RECOMMENDATIONS

4.1 Screening of Polymers

Based upon the experience and information acquired during this program, it is believed that there is no reliable method immediately available for assessing the relative cryogenic effectiveness of a polymer in unprocessed, granulated, or pelletized form for the required end application as a film. The reason is that biaxial orientation processing of a film appears to have a marked effect on the film's dynamic mechanical properties at both cryogenic and room temperature, as indicated in part under this program and by others.[8] Accordingly, conclusions drawn from any specific dynamic mechanical test or tests on the polymer in unprocessed, granulated, or pelletized form may not be applicable to the fabricated film in an oriented state.

The most practical approach would appear to involve several considerations such as:

a. Availability of monomers and difficulty of polymer synthesis. It is one thing to propose an interesting polymer structure and another to find that little is known about its synthesis in high molecular weight. In brief, it would be best to study a few polymers by way of carefully selected changes in basic structure.

b. Film-forming ability of polymer. Can the polymer be formed into a coherent, homogeneous film of uniform and controlled thickness? A polymer of very high softening temperature which is also insoluble in any known solvent could neither be melt-pressed, extruded, nor solvent-cast into films. Also, a polymer which is too low in molecular weight may give tacky or non-coherent films. Finally, the molecular length distribution may also be very important; hence, the need for determining weight and number average molecular weights.

c. Biaxial orientation properties. What latitude does the film have in terms of various stretching variables?

These practical considerations, by themselves, entail an appreciable amount of work. Furthermore, they provide a successive type of screening wherein at any stage a candidate polymer could be eliminated from further evaluation (in terms of its various physical properties of interest).

4.2 Criteria in Selection of Polymers for Study

4.2.1 Rubbers and Elastomers

Rubbery and highly elastomeric polymers do not appear desirable for application in this program, primarily because they are brittle solids below their Tg. Effective biaxial orientation of such materials does not appear

possible because of the natural tendency of such polymers for extensive entanglements in their amorphous rubbery state. Uniaxial orientation is possible, but this may not be sufficient to provide the requisite strength for three-corner folding. It is felt that if such a polymer could be biaxially oriented, the resulting film would be too taut for the desired application.

4.2.2 Biaxial Orientation

Based in part upon our studies as well as on various theoretical considerations, the ability of a polymer film to be biaxially oriented appears to be highly desirable in order to obtain a useful film for the desired cryogenic application.

4.2.3 Semicrystalline Polymers

Polymers capable of possessing some crystallinity combined with their amenability to biaxial orientation appear the most promising types for this application. For this purpose, two approaches can be taken regarding the selection and use of desirable polymer structures.

a. Highly ordered structures

b. Partially rigid structures, e.g., benzene rings in the backbone of the polymer such as Kapton.

The partially rigid type of polymer may also have a tendency for crystallization though it is presently considered as a separate distinctive characteristic of a polymer. Very high rigidity would favor the formation of highly intractable, polymers with melting points too high for biaxial orientation. "Moderate" rigidity features, such as conferred by the benzene rings in poly(ethylene terephthalate), on the other hand, appear desirable.

4.3 Specific Polymers of Interest

Based in part from what was learned in this program and in part from literature information, the following classes of polymers are recommended for study.

a. Polyesters

b. Poly 2,6-dialkyl phenylene oxides

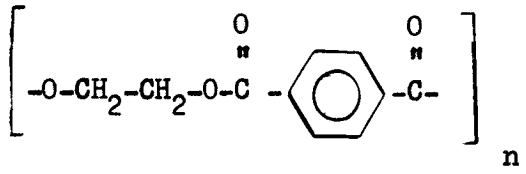
c. Polyphenylene siloxanes

d. Polypyromellitimides

These four classes are discussed in the following subparagraphs.

4.3.1 Polyesters

Poly(ethylene terephthalate) (I)



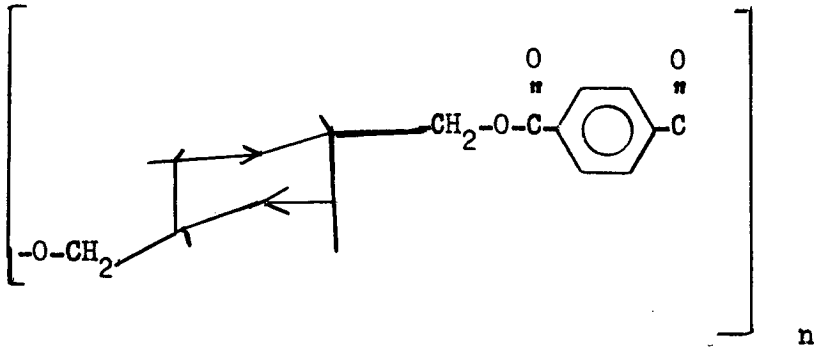
(I)

This polymer available in the various types of Mylar films was studied, and, in particular, the effect of biaxial orientation parameters on twist-flex life and other properties was partially defined. It was found that these biaxial orientation parameters have a profound influence on twist-flex life as well as on tensile strength properties. Films were prepared that were superior to Mylar C in twist-flex performance at liquid nitrogen temperatures. These films possessed higher stretch ratios than Mylar C film.

In addition another commercial form of this polymer, Mylar T, was found to be superior to Mylar C in twist-flex life at liquid nitrogen temperature. Mylar T differs from Mylar C in the way in which it is oriented.

Additional work should be carried out in studying the effect of biaxial orientation parameters, specifically the degree of stretch and the temperature of stretch on the resultant properties of this polymer.

Poly(4-4'-cyclohexylene dimethylene terephthalate) (II)

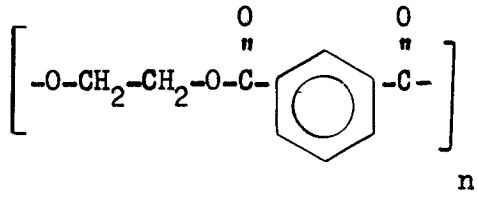


(II)

The commercial form of this polymer is produced by Tennessee Eastman and is known as Kodar. It is presumably prepared from a mixture of the cis and trans forms of 1,4 cyclohexylene dimethylene diol, for economic reasons.

Cost-effectiveness is undoubtedly the key reason for using the mixture. Kodar itself has been evaluated for cryogenic twist-flex life and was found to be inferior to Mylar C. On the other hand, there is no a priori reason to expect at this time that the basic polymer structure could not be biaxially oriented under different conditions than Kodar to provide an improved cryogenic film.

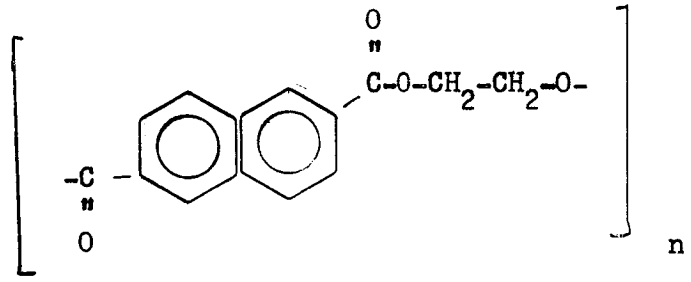
Poly(ethylene isophthalate) (III)



(III)

This polymer was synthesized, biaxially oriented (4 x 4 stretch ratio) and evaluated during this program. It is recommended that further work be carried out on this polymer and on copolymers of it with poly(ethylene terephthalate).

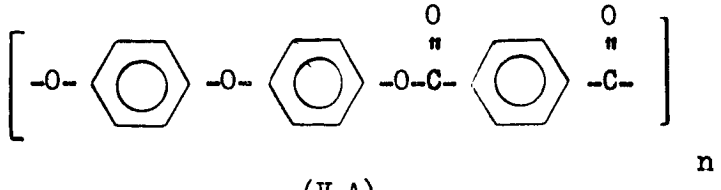
Poly(ethylene 2,6-naphthalene dicarboxylate) (IV)



(IV)

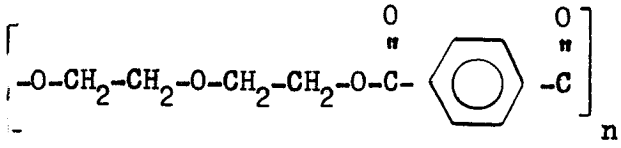
This polymer can be fabricated into films quite comparable to Mylar C, with respect to ambient temperature applications.

Poly(4,4'-diphenyloxy terephthalate) (V-A)

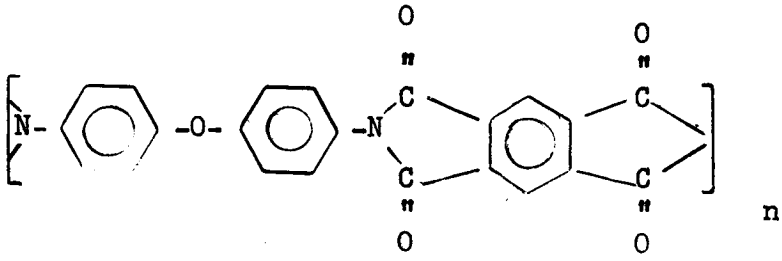


(V-A)

This polymer should be less elastomeric than poly(diethylene oxyterephthalate) and more processable than Kapton.

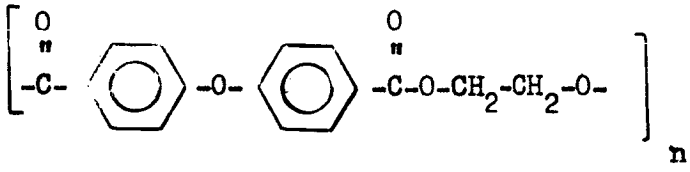


poly (diethyleneoxy terephthalate)



Kapton

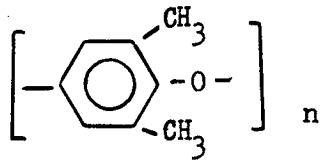
Poly(ethylene 4,4' -Oxy-diphenyl dicarboxylate) (VI)



(VI)

This polymer might yield more flexible films than poly(ethylene terephthalate) because of the additional flex point (the oxygen between the phenylene rings) in the backbone. Alternatively, one could prepare copolymers of this material with PET by the use of appropriate monomers.

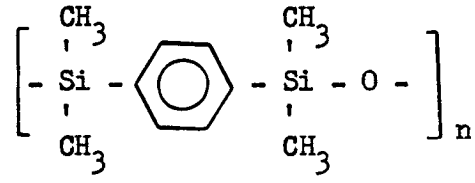
4.3.2 Poly(2,6-dimethyl phenylene oxide) (PPO) (VII)



(VII)

This polymer, obtained from the General Electric Co. was solvent cast into 0.7- to 1.5-mil films which were found to yield fair twist-flex performance at -195°C. Melt pressing however did not yield suitable films for biaxial orientation. The following approaches are recommended for further studies: (1) extrusion of amorphous film for biaxial orientation, and (2) solvent casting of uniform 1/2-mil films for testing.

4.3.3 Poly(4,4'-phenylene-bis(dimethylsiloxane)) (VIII)

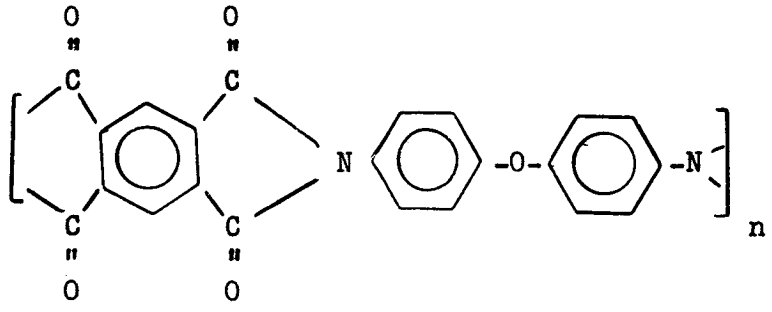


(VIII)

This polymer reportedly yields tough orientable fibers and films (c.f., U.S. Patent 2,562,000, du Pont) and can be prepared from the commercially available monomer. This polymer was prepared in small quantities during this program but time did not permit the synthesis of larger quantities and subsequent evaluation of films for cryogenic applications.

4.3.4 Polypromellitimides

Poly 4,4' -diphenyl oxy pyromellitimide Kapton (H-Film) (IX)



(IX)

4.4 The Twist-Flex Method

Based on the knowledge gained during the course of this program Melpar recommends the following in regard to twist-flex testing:

a. A minimum of 20 specimens of each film under evaluation should be tested. This is required in order that a cycles-to-failure value can be obtained with greater reliability.

b. Film specimens of the 4 inch by 4 inch size should be tested. This is recommended since the 4 inch by 11 inch films give a very high level of scatter and thus make the task of assigning a cycles-to-failure value to a specific film sample quite difficult. For relative comparisons between different film samples this smaller size is adequate.

c. Twist-flex testing at a single frequency, e.g., 9 cycles/minute, which may not correspond to the frequencies encountered in actual practice, may be misleading. It is recommended that twist-flexing at both a higher and lower frequency be studied.

5. REFERENCES

1. Pope, D. H., Killian, W. R., and Isakson, V. E., Positive Expulsion of Cryogenic Liquids, Phases I and II, Final Reports, NASA Contract NAS9-513, June 1962 - June 1963 and June 1963 - June 1964, Beech Aircraft Corporation, Boulder Division, Boulder, Colorado.

2. Mylar is the registered trademark of the E.I. duPont Company for their poly (ethylene terephthalate) film.

3. Nomex-Nylon paper is an experimental high temperature resistant nylon material prepared by the E.I. duPont Company.

4. Dacron is the registered trademark of the E.I. duPont Company for their poly (ethylene terephthalate)fiber.

5. Lucas, W. R. and Riehl, W. A., ASTM Bulletin, No. 244 February 1960, pp 29-34.

6. Sorenson, W. R. and Campbell, T. W., Preparative Methods of Polymer Chemistry, Interscience Publishers Inc., New York, 1961, pg. 112.

7. Kolb, K. E., U. S. Patent 2,901,505 (1959).

8. Heffelfinger, C. J. and Schmidt, P. G., The Structure and Properties of Oriented Polyethylene Terephthalate Films, Paper 326, 53rd National Meeting A.I.Ch.E. May 17-20, 1964, Pittsburgh, Pennsylvania.

9. Statton, W. O., J. Appl. Polymer Sci., 7, 811-13 (1963).

10. For example see: Pangonis, W. J., and Simril, V. L., U. S. Patent 2,851,733 (1958); Alles, F. P. and Heilman, K. A., U. S. Patent 2,728,941 (1956); duPont, British Patent 921,308 (1963); Imperial Chemical Industries, British Patent 887,687 (1962).

11. Schulken, R. M., Boy, R. E. and Cox, R. H., Differential Thermal Analysis of Linear Polyesters, ACS. Polymer Preprints, Vol. 4, No. 2, page 453, September 1963 (New York meeting).

12. Private communication from E.I. duPont and Company.

APPENDICES

APPENDIX A - LITERATURE SURVEY

APPENDIX B - BROAD-LINE NMR APPARATUS

APPENDIX C - MEETINGS WITH CONSULTANTS

APPENDIX A
LITERATURE SURVEY

1. State of the Art Literature Survey

Part A - Cryogenic Testing of Commercial Polymers and Theories Concerning the Glassy State
Part B - Synthesis and/or Modification of Polymers Including Orientation and Permeability

List of Literature Surveyed:

1. International Aerospace Abstracts, January 1, 1964, to April 1, 1964.

2. Scientific and Technical Aerospace Reports, January 1, 1963, to March 31, 1964.

3. Technical Publications Announcements, April to December, 1962.

4. Index of NASA Technical Publications, July 1960 to December 1961.

5. Technical Abstract Bulletin, January 1, 1957, to May 1, 1964.

6. Chemical Abstracts, January 1, 1957, to December 31, 1963.

Key Words:

Cryogenic(s) (Plastics, films, adhesives, etc.)
Low Temperature (Plastics, films, adhesives, etc.)
Polymers, Plastics, Polymerization, for Cryogenic Temperatures
Synthetic, Synthesis (Materials for Cryogenic Temperature)
Mylar - polyester films - biaxial orientation.
Grafting on Mylar, Silicone, Fluorocarbons.
Copolymers of Poly(Ethylene Terephthalate), Silicone Polymers and Fluorocarbons.

Part A. Cryogenic Testing of Commercial Polymers and Theories Concerning the Glassy State

APPENDIX A

LITERATURE SURVEY

1964

1. Toth, J. M., Jr.
"Barrier Films for Filament-Wound Fiberglass Cryogenic vessels"

Advances In Cryogenic Engineering, Vol. 9, page 537,

Plenum Press, New York, 1964.

The requirements for a liner for a fiberglass, filament wound, cryogenic propellant tank include impermeability to the cryogenic fluid and non-reactivity with either the fluid or the gas.

In this article the author reports on the results of tests on a rather large number of metals, metal-plastic laminates and plastic materials. Such materials as aluminum foil, lead foil, aluminized Mylar, FEP/Aluminum, Dacron/Aluminum-Mylar/Dacron, Saran, Kynar, Mylar, Aclar, Teflon, urethane-Epoxy laminate, etc., were tested to determine suitability for liner applications. Contraction behavior of bonded specimens was determined in liquid hydrogen and uniaxial strain compatibility tests were made with tensile specimens in liquid nitrogen and liquid hydrogen. The liner materials were bonded to the fiberglass composite and cycled at varying percentages of the ultimate loads. In liquid nitrogen, the polymeric films performed satisfactorily, while all of the metals showed high residual elongation, debonding, and cracking. In liquid hydrogen, Mylar performed best among the plastics tested.

1963

2. **Lenel, F. V. and Ansell, G. S.**

"Metals, Ceramics, Polymers - Interdisciplinary Aspects of Sintering and Plastic Deformation".

I&EC. 55, 46 (November 1963) (From a Symposium on "Materials" held in Boston, Mass. in 1963; Sponsored by Llikon Corp of Natick, Mass.)

One of the most challenging problems facing technologists today is that of finding methods for predicting behavior of materials under different environments and stress conditions.

When stress is applied to materials, the total amount of deformation is composed of three parts: elastic, anelastic and plastic. The instantaneous elastic and time dependent anelastic portions are both recoverable, i.e., disappear when the stress is removed. The plastic deformation occurs over a period of time and remains even after the stress is removed. This article gives a qualitative description of current theories concerning transport phenomena in materials. Details are omitted and no references are cited.

3. Robins, R. F., Ohori, Y. and Weitzel, D. H.
"Linear Thermal Expansion of Elastomers In the Range 300° to 76°K."

Advances In Cryogenic Engineering, Vol. 8, page 287

Plenum Press, New York, 1963.

In the search for reliable, simple low temperature static seals a large number of representative elastomers were tested for thermal expansion properties over the range 76° to 300°K. These materials were conveniently placed in 5 groups representing families of elastomers. These groups were the fluorocarbons, butadiene copolymers, isobutylene-isoprenes, natural rubber and neoprene and silicone rubbers.

The authors point out that the silicones are perhaps the most promising group for future investigations for cryogenic applications. Dimethyl silicone rubber when modified with 30 mole% of vinyl had the lowest Tg found to date, 146°K. The straight dimethyl silicone rubber had a Tg of 156°K.

4. Bailey, D. C., Holland, W. D. and Hulsebos, J.
"Hydrogen Permeation Measurements on Vapor Barrier Materials for Cryogenic Insulations".
Society of Automotive Engineers, National Aeronautic and Space Engineering and Manufacturing Meeting, Los Angeles, Calif., September 23-27, 1963., 746D

This paper describes a method for measuring hydrogen permeabilities of plastic films and metal foils. The method utilizes a hydrogen mass spectrometer leak detector. Hydrogen permeability values of several plastic films are presented over a temperature range of 250 to -150°F.

It is known that the factors influencing the permeability of plastics are temperature, chemical structure, degree of crystallinity, and any superimposed stresses. This paper deals only with the effect of temperature.

Materials tested included the fluorocarbon films. (FEP, KEL-F, Tedlar). Mylar, polyethylene and H-Film (polyimide). Activation energies and constants of permeation were determined for these materials.

5. Brzeski, S. J., Brubel, F. W., Jr., Hoffman, J. C., Fletcher, J. M. and Lipke, L. M.
Task 4. MPU Bladder Development, Second Quarterly Progress Report.
Contract AF04 (693)-273
Program 706, Radio Corporation of America, Defense Electronic Products, Burlington, Mass.

The purpose of this task was to develop a non-metallic positive expulsion bladder to be used in space vehicle propulsion systems,

utilizing N_2O_4 and a 50/50 blend of UDMH and N_2H_4 as the propellants.

Full scale bladder tests have shown that both a "bag-in-bag" single layer Teflon film combination and a single "bag" Teflon film combination fail during propellant expulsion tests below 70°F. These results indicated a need for additional investigations into the mode of failure and a better correlation between material sample tests and full scale bladder tests.

1963

6. Ruby, J. D.
"Evaluation of Elastomers for Potential Use at Cryogenic Temperatures"
DA Project No. 1-H-0-24401-A-110
AMC Code No. 5026.11.842
Report No. 63-1537, Rock Island Arsenal, Rock Island, Ill.

The purpose of this work was to determine the lowest temperature at which a variety of rubber vulcanizates and other non-metallic materials would remain non-brittle and flexible and exhibit moderate recovery from applied deformation.

Materials such as methyl phenyl siloxane, methyl phenyl vinyl siloxane, fluorosilicone, synthetic and natural rubber, butadiene (92)-styrene (8) rubber, ethylene-propylene rubber, cis 1,4 polybutadiene, polyurethane, carboxy modified polybutadiene, strap and harness leather, cordovan leather, and kraft paper were evaluated as elastomers at low temperatures.

Only three of the synthetic materials tested remained sufficiently flexible at -100°F to be considered servicable at this temperature. These were the methyl phenyl silicone, methyl phenyl vinyl silicone and cis 1,4 polybutadiene. The leather and paper materials showed exceptional non-brittle and flexible properties at -300°F.

The author feels that the best approach to obtaining a truly cryogenic elastomer resides in modification of the leather or cellulose to impart elasticity to them since they possess flexibility at liquid nitrogen temperatures.

1963

7. Wegner, U.
"Theoretical Investigations of The Behavior of Brittle Materials at Various Ranges of Temperature"
Contract No. AF61(052)-280; Project No. 7350, Task No. 735003
(University of the Saarland, Saarbrucken, Germany)

A new theory of elasticity was developed which will provide a mathematical treatment of the behavior of brittle materials. By postulating two axioms concerning the invariance of the deformation energy under any coordinate transformation and the continous transition of the volume

dilation from the elastic to the plastic range it is possible to establish a general invariant non-linear stress-strain relation for the three-axial state of stress.

To demonstrate the capability of the new theory some problems of plasticity which are of practical interest are treated.

1962

8. Miller, R. N., Bailey, C. D., Freeman, S. M., Beall, R. T., and Coxe, E. F.
"Properties of Foams, Adhesives and Plastic Films at Cryogenic Temperatures."
I&EC, Product Research and Development, Vol. 1, No. 4, 257 (December 1962)

The mechanical properties of selected foams, adhesives and plastic films were evaluated at -320° and -423°F. The films were tested for tensile and elongation properties as potential vapor barrier materials at -320°F. Specifically, 3 mil Mylar (polyester), 4 mil Tedlar (poly(vinyl fluoride)) and 3 mil Aclar (fluorohalo-carbon) were tested. The Mylar film was the strongest of the materials tested having a tensile strength of 44,000 psi in longitudinal direction. In a transverse direction, the average strength was 45,600 psi. The Tedlar film had an average strength of 33,600 psi, while the strength of the Aclar film was only 11,500 psi at -320°F.

9. Hunter, B. J., Bell, J. E. and Penner, T. E.
"Expulsion Bladders For Cryogenic Fluids"
Advances in Cryogenic Engineering, Vol. 7, page 155, Plenum Press, New York, 1962

Materials for constructing expulsion bladders for use with cryogenic fluids can be evaluated by using criteria such as flexibility at cryogenic temperatures, tensile and tear strength, permeability and ease of fabrication. Other factors to be considered include density, thermal conductivity, compatibility with various cryogens, impact sensitivity with liquid oxygen and the effects of various types of radiation.

Several tests were carried out on bladders constructed of various materials. These included various gauges of Mylar, Type A, alone or laminated with such substrates as nylon and dacron.

The results obtained were as follows: triple membranes, each acting individually, of 1/4 to 1/2 mil Type A Mylar are capable of withstanding the flexing and folding required for the expulsion of liquid hydrogen,

nitrogen and oxygen. Exceptional performance during advanced endurance testing, together with such considerations as tensile strength and permeability, suggest that 1/2 Mil Mylar is quite suitable for expulsion bladders.

10. Bell, J. E., Killian, W. R., Penner, J. E., Pope, D. H., Sutton, H. E., and Tweed, R. M.
"Development of Positive Expulsion Systems for Cryogenic Fluids"
Final Report - Phase II and III
Contract AF33(616)-6930, Project No. 3084, Task No. 30273
Beech Aircraft Corporation, Boulder, Colorado.

A large number of films were tested on a mechanical flexing apparatus at liquid nitrogen temperatures. This was done since if a material was incapable of flexing at 77°K, it certainly would not perform any better at 20°K. Over 75 samples were so tested with only 4 materials passing this test. These were Mylar (Type A, 1/2 mil and 1 mil), vacuum deposited aluminum on Mylar, and various laminates of Nylon-Mylar and Dacron-Mylar), Teflon FEP (1/2 mil and 1 mil; also a laminate of 21 oz Teflon felt to both sides of 5 mil Teflon FEP film), Trithene (Type A, 2 mil) and Kel-F (Grades 270 and 300), unplasticized.

Films that were rated as marginal were Teslar (PVF film), Scotchpak (MMM polyester) and several developmental films.

Films that failed included polyethylene, cellulose acetate, cellulose acetatebityrate, polyvinyl fluoride, vinyl chloride, polyester film (Cadillac Plastic and Chemical Co.,) and nylon. A 1/2 mil aluminum foil showed ductility but developed pin holes.

Preliminary tests conducted during Phase I or a 1/2 mil Mylar, 3 membrane bladder showed the feasibility of this type of positive expulsion system (79 cycles without failure). During phase II however, one bladder failed after 20 cycles, a second bladder failed after 2 cycles, and a third bladder failed after 1-1/2 cycles.

The authors point out the need for many more tests on bladders of different types and sizes to provide significant statistics relative to the reliability of bladders for space applications.

11. Brink, N. O.

"Determination of the Performance of Plastic Laminates Under Cryogenic Temperatures"
Contract No. AF33(616)-3289, Project No. 7381, Task No. 738103
Narmco Research and Development, San Diego, California

The objective of this program was to determine the performance of various reinforced plastic laminates at different cryogenic temperatures. Ten materials were evaluated, and represented the epoxy, phenolic, polyester, high temperature polyester, and silicone resin system. The materials were tested in tension, compression, flexure, and tensile fatigue. Test temperatures included room, -110°F (dry ice-alcohol), -320°F and -423°F.

Results of this program have shown that the reinforced plastic materials generally increased in strength as the temperature decreased. The laminates maintained the same relative tensile fatigue resistance at the cryogenic temperatures tested when compared to the room temperature results.

12. Haskings, J. F., Hertz, J. and Campbell, M. D.
"The Determination of Thermophysical Properties of Plastic Materials and Composites at Cryogenic Temperatures"
Contract No. AF33(657)-9160; Quarterly Progress Report No. 1
1 October 1962. (General Dynamics)

This initial report contains data on the tensile properties, density and coefficient of thermal expansion of poly (ethylene terephthalate) (Mylar). Tensile properties were measured at 78°F.

A survey was made of industry to ascertain which composite cryogenic insulations look most promising. Initial results of that survey are presented.

A list of the materials whose low temperature properties are to be evaluated during the course of the contract is given.

1961

13. Lieb, J. H. and Mowers, R.

"Problems in Evaluating and Testing Plastics"
Materials in Design Engineering, 54, 115 (July 1961)

One of the most important factors revealed in this study was the dependence of mechanical properties of plastic materials at cryogenic temperatures upon the crystallinity of the material. Since crystallinity of plastic materials is critically dependent on final design shape and processing history, the mechanical properties of test specimens with a certain crystalline content will not be indicative of the mechanical properties of a molded or extruded part of a different crystalline content.

Among the limited number of plastics retaining some ductility at cryogenic temperatures are the fluorocarbons, e.g. TFE (Teflon), FEP (Teflon X-100) and CFE (Kel-F). At -320°F the low crystallinity, high amorphous content fluorocarbons are stronger and more ductile than the highly crystalline materials. For specimens of small cross-section (e.g., less than 1/8 in. thick) this is not a problem since samples with almost any degree of crystallinity desired can be produced. Rapid quenching from above the melting point produces minimum crystallite formation; gradual cooling results in maximum crystallite growth. This is not the case with thicker specimens where even rapid cooling does not lead to lowered crystallinity due to the insulating action of the outer skin upon the inner section of the specimen.

A method for relating crystallinity to hardness was developed. It was found that this method was able to yield degree of crystallinity data with the accuracy and sensitivity of the X-ray diffraction method.

14. Stein, M. and Hedgepeth, J. M.

"Analysis of Partly Wrinkled Membranes"
Technical Note D-813, National Aeronautics and Space Administration, Langley Research Center, Langley Field, Va., July 1961

A theory is derived to predict the stresses and deformations of stretched-membrane structural components for loads under which part of the membrane wrinkles. Rather than studying in detail the deformations in the wrinkled region, the present theory studies average displacements of the wrinkled material. Specific solutions of problems in flat and curved membranes are presented. The results of these solutions show that membrane structures retain much of their stiffness at loads substantially above the load at which wrinkling first occurs.

15. Sirocky, P. J.

"Transfer of Cryogenic Fluids By An Expulsion Bag Technique"
Technical Note D-849; National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio

Tests were run to demonstrate the feasibility of transferring cryogenic fluids by means of an expulsion-bag technique. Mylar-coated bags used as fluid containers were found to be flexible enough to collapse at temperatures of approximately 36°R and thereby cause expulsion of the fluid. Visual inspection and helium gas pressurization of the bags showed no damage even after repeated cycles.

Two different bags with 1/2 and 1 mil Mylar coatings on a 5 mil Dacron cloth were used in these tests. Seven cycles were made with liquid nitrogen and six cycles with liquid helium. Visual inspection and pressure testing with helium gas showed no signs that material damage had occurred.

16. Tadashi Sugawara (Tokyo U.)
"Properties of Matter at Extremely Low Temperatures"
Kagaku (Tokyo) 30, 222-7 (1960)

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17. R. P. Reed and R. P. Mikesell (NBS Colo)
"Some mechanical Properties of Mylar and Dacron Polyester Strands at Low Temperatures"

Rev. Sci. Instr., 29, 734-6 (1958)

Interwoven strands of Dacron polyester fiber and Mylar polyester sheet have been tested in tension and impact at 4 temperatures: 296°K, 228°K, 195°K, and 76°K. Results were graphically illustrated and indicated that Dacron strands in tension were as strong at 76°K as at room temperature, while strands of Mylar became considerably weaker at lower temperatures. Also the strands expanded, indicating a negative coefficient of expansion.

18. F. A. Marzio and J. H. Gibbs (American Viscose)
"Glass Temperature of Copolymers"
J. Polymer Sci, 40, 121-31 (1950)

By considering the configurational entropy and configurational energy of the polymer chain as a function of chain flexibility (fractions of bonds rotated out of their lowest energy configuration), a second order transition is predicted, which has the properties of the observed glass transition. On the basis of simplifying assumptions, the theory leads to an expression for predicting the transition temperature of copolymers from those of the homopolymers. In a polymer such as the polyester made from ethylene glycol, terephthalic acid, and adipic acid, where A-B links are the same as A-A and B-B links, the agreement between theory and the data of Edgar and Will is close.

Part B. Synthesis and/or Modification of Polymers
Including Orientation and Permeability Data

1963

1. Maurice Prober
"Co-vulcanized Fluorinated Polyacrylate Elastomers and Organo Polysiloxane Gums"
(GE) U.S. 3,069,378 (1962)

The elastomers contain the recurring unit, $-CH_2-CH(CO_2CH_2R)-$ where R is a perfluoro akyl or alkoxy radical. The products are resistant to polar and non-polar solvents and oxidative degradation, have good low temperature flexibility, and can be bonded.

2. Heinz R. Niebergall - Brit 916,260 (1963)

"Polymers from Terephthalates or Terephthalamides and Organo-Tin or Organo Silicon Compounds"

Polymers are formed by reaction of substantially equimolecular proportions of an unsaturated derivative (ester or amide) or terephthalic acid and a diorgano tin or diorgano silicon compound.

3. Ichiro Sokurada, Yasuhiko Nukushina & Taisuke Ito (Kyoto Univ.)
"Experimental Determination of the Elastic Modulus of Crystalline Regions in Oriented Polymers"
Kobunshi; Kagaku 19, 285-92 (1962)

E of the crystalline regions of highly oriented specimens of poly (ethylene terephthalate) (I), poly (vinylidene chloride), and cellulose (III) were: 76, 41.5 and 137 x 10^4 kg/sq.cm. respectively.

4. Mario Baccaredda (Pisa Univ., Italy)
"Crystallinity and Mechanical Properties of High Polymers"
Chem. Ind. (Milan) 44, 1383-9 (1962)

Youngs modulus, E, (determined through sound velocity measurements at medium frequencies) and internal dissipation Q^{-1} (Q being the resonance coefficient) were measured at different temperatures for various types of polymers. The resulting diagrams show clearly first and second order transitions. E increases with the degree of crystallinity. The influence of thermal treatments on crystallinity were studied for poly (ethylene terephthalate).

5. Bacon Ke (Amoco Chemical Co.)
"Differential Thermal Analysis of High Polymers IV. The Saturated Linear Polyesters"
Journal of Applied Polymer Science 6, 624-8

Differential thermal analysis of quenched poly (ethylene terephthalate) (I) showed the following phase changes: glass transition at 70°, "cold" crystallization at 100-25°, premelt crystals at 220°, and melt at 265°. An annealed sample gave only the melting peak. From the area under the peak and from the percent crystallinity, the heat of fusion of the crystals was calculated as 27.8 cal/gram. Substitution of some (HO, CH_2 CH_2)$_2$O for HO CH_2CH_2 OH in the preparation of the polymer lowered the transition temperature. Thermograms of terephthalate copolymers made with 10 mole % 1,3 on 1,4-cyclohexylenedimethanol were generally similar to those of copolyester made by substituting 40 mole isophthalic acid for terephthalic acid showed no crystallization above the glass transition temperature. Thermograms of Dacron filament and Mylar film, and poly (1,4-cyclo hexylene-dimethylene terephthalate) (Kodel) showed these polymers to have high degrees of crystallinity.

1962

6. V. V. Chernaya and R. L. Vol'chenko
"Means of Improvement of Cold Resistance in Polymers"
Uspekhi Khim 31, 336-50 (1962)

A review with 78 references through 1960 covers plasticization as a means of lowering the glass temperature and copolymerization and modification methods for decreasing the t endency toward crystallization in polymers.

7. B. Kanner and W. G. Reid
"Graft Copolymers of Fluoro olefins with Dimethol Silicones"
Am. Chem. Soc., Div. Polymer Chem., Preprints 2, No. 1, 99-104 (1961)

Dimethyl silicones react with CH_2:CF_2 and CF_2:CFCl in the presence of a di-tert-Butyl Peroxide Catalyst with the formation of silicone-fluorocarbon graft copolymers. Elastomers prepared from these gums had markedly improved resistance to swelling by hydrocarbon solvents. The preparation of silicone and flyorocarbon, as well as the molecular weight of the graft polymer are readily controlled.

8. Janas Dobo, Agnes Somogyi and Laszlo Kiss
"Grafting (Styrene) onto Poly (Tetrafluoroethylene)"
Magyar Kem. Folyairat 68, 121-4 (1962)

Styrene was grafted onto the surface of previously irradiated poly (tetrafluoroethylene) II at approximately 50°.

If the radiation had a low intensity (ca. 1 megar) the grafting progressed into the interior of II at a rate of 20-30 μ/hr.

9. A. E. Woodward (Pa. State Univ.)
"Transitions and Segmental Motion in High Polymers"
Trans. N.Y. Acad. Sci. 24, 250-61 (1961)

Nuclear Magnetic Resonance, dynamic mechanical loss, and storage modulus are well suited for studying the principal glass transformation in the amorphous and partially crystalline polymers.

NMR is sensitive for studying side chain rotations and oscillations, especially methyl group rotation.

The dynamic mechanical method is the most suitable for the study of certain secondary transitions that appear to involve principally limited main chain oscillations.

10. Brian F. Jennings
"Copolyesters" Brit 897,640 (1962)

Copolyesters of isophthalic and terephthalic acids with a bis phenol other than 2,2-bis(4-hydroxy phenyl) propane are prepared.

11. John Farago
"Graft Copolymers of Polyurethanes with Acrylic Polymers"
U.S. 3,038,876

A solution of an addition polymer such as acrylonitrile homo polymer or copolymer with methyl acrylate is mixed at 0° with a solution in the same solvent of bis(4-isocyanatophenyl) methane or other similar compounds. Reaction occurs at 0° to form a graft comprising addition and condensation polymer segments. Other addition polymers (elastomers) may be used as substrates. The compounds are useful in strong, clear, homogeneous fibers, films and filaments.

12. Donald Leroy Bailey and Francis M. O'Connor
"Organo Silicone Block Copolymers"
Brit 880,022 (1961)

Linear organosilicone block copolymers of the general formula $R'O\left[(R_2SiO)_x\right]_a\left[(C_nH_{2n}O)_y\right]_b R'$ are described.

13. Coleman J. Major and Karl Kammermeyer
"Gas Permeability of Plastics (and rubbers)"
Mod. Plastics 39, No, 11, 135, 138, 140, 142, 145-6, 179-80

The permeability and its temperature dependence to one or more of the gases CO_2, O, N, C_3H_8, air and He was determined for Adiprene, brominated

butyl rubber, cellulose acetate butyrate, Delrin, Epon 1001, Hysol, a polycarbonate resin, Mylar, Penton, Phofilm, polyethylene, Cryovac-L film (irradiated, monoaxially and biaxially oriented) polystyrene (biaxially oriented), poly (vinyl butyral) Butuar B-76, poly (vinyl chloride) Saran, silicone rubber (Silastic), RTV-90, LS-63, nitrile rubber, thickol rubber, a urethan resin, and a vinylidene fluoridehexafluoro propylene copolymer.

14. John E. Saville (GE)
"Silicone-Polyester Copolymers"
U.S. 3,044,979, July 17, 1962; U.S. 3,044,980

Heat Curable silicone-polyester copolymer compositions are prepared by copolymerizing suitably hydrolyzed silanes with an OH rich polyester made by the reaction of (a) 25-60 equivalent percent of a lower dialkyl ester of isophthalic acid, terephthalic acid and their mixtures (b) 10-50 equivalent percent of ethylene glycol (I) and (c) 20-60 equivalent percent of a saturated aliphatic polyhydric alcohol having at least 3 OH groups.

15. S. N. Borisov, A. V. Karlin, L. M. Chudesova, F. A. Galil and L. M. Chebysheua
"The Properties of Ethyl Phenyl Siloxane Rubbers"
Kauchuk i Rezna 21, No. 6, 3-6 (1962)

To reduce the tendency for crystallization at low temperatures, diethyl-(I), methyl phenyl (II) and ethyl phenyl siloxane (III) were copolymerized with dimethyl siloxane. The best low temperature properties were produced when I, II, and III were used in concentrations of 7-8 mole percents. Properties are compared in tabular form.

16. "Polyester Film" (Goodyear Tire & Rubber Co.)
Brit. 877,540

Unstretched, amorphous films of linear, aromatic polyester resins, e.g., ethylene terephthalate (I) ethylene isophthalate (II) copolymers are processed at temperatures above the glass transition but below the sticking temperature. This avoids the formation of cracks and stresses during folding or other severe stresses. The glass transition temperatures of copolymers of (I) with 10, 20, 30 and 40% II are 71°, 68°, 64.5°, and 61°.

17. Gerald Oster
"Improvement of Plastics by UV Light"
Large Radiation Sources in Ind., Proc. Conf., Warsaw 1959, 1, 321-9 (1960)

The use of ultraviolet light for cross-linking and surface grafting of polymers is described. Acrylamide was grafted onto poly(ethylene terephthalate) film.

18. M. Alliot - Lugaz
"Photographic Film Supports by Grafting Acrylic Acid on Poly(ethylene terephthalate)"
Fr. 1,263,842

Biaxially oriented poly(ethylene terephthalate) treated during 5 hours at 50° with air containing 55 mg/liter O_3 at a rate of 200 l/hr., coated with acrylic acid (to correspond to 4g/sq. meter) and held 1 hour at 60° under N_2 gave a support to which gelatin adhered readily.

1961

19. Leroy Frederick Gronholz
"Biaxially Elongating Thermoplastic Polymeric Films"
(to E.I. duPont de Nemours & Co) U. S. 2,968,065 Jan. 17, 1961

Crystallizable title films are elongated in a continuous process in the transverse direction and the longitudinal direction by stretching at controlled temperatures which are related to the second order transition temperature (a) and the crystalline melting temperature range (b) of the polymer being stretched. Examples of polymers which can be stretched are poly(ethylene terephthalate) (I), poly(hexamethylene adipamide) and poly caproamide.

The steps in this process are (1) elongating the amorphous, polymeric film in 1 direction at a temperature T, between temperature (a) and a temperature 35° above (a), (2) subjecting the film to a temperature of 25° above T. to just below temperature (b) while tension is maintained in a direction at a temperature range of 130° below to 30° below temperature.(b).

A balanced film having equivalent tensile properties in both directions may be produced by this method when the specified temperatures are maintained and the first elongation is 2.5 - 4.0X while the second is only 1.3 - 1.9X, in which X is the original dimension of the film.

20. Robert L. Miller and Lawrence G. Nielsen
"Crystallographic Data for Various Polymers"
J. Polymer Science, 44, 391-5 (1960)

A table and 60 references.

21. Janis A. Bungs
"p-Xylenediol Polyesters"
U.S. 2,967,854 (Diamond Alkali Co.)

Polyesters useful in the manufacture of fibers, films, castings, or laminates are prepared by treating a diol, made by side chain halogenation

of p-xylene followed by hydrolysis with a diacid, a diester, or a dihalide of a dicarboxylic acid. An especially suitable diol is p-xylenediol and an especially useful compound is made from it and dimethyl terephthalate. Strong and elastic fibers can be drawn from this melt.

22. Orin C. Keplinger, Otto C. Elmer and Joe Duncan
"Rubbery Reaction Products of Organic Polyisocyanates and Dihydroxy-terminated Polyesters"

Easily curable rubbery polyester-urethan compositions having improved low-temperature brittle points are prepared from approximately equimolecular amounts of a polyester and a polyisocyanate. The polyester is prepared from a mixture of 1,4-butylene glycol (I) and ethylene glycol (II). It should comprise between 30 and 70 mole percent of the glycols to insure a low brittle point, a high degree of non-stiffness at low temperature and/or easily curable polyurethan.

23. Ceci Louis Long (duPont)
"Biaxially Oriented Polyester Films"
U.S. 2,968,067

Films of poly(ethylene terephthalate) are oriented by stretching longitudinally at 70-120° while moving under lateral tension to avoid contraction, then stretching the film laterally at 70-120° to biaxially orient the film. The film is then held for 0.005 - 5 minutes in a zone heated to 25° and to at least 10° below the subsequent heat setting temperature. The film is finally heat set by heating at 150-230° without allowing shrinkage. The process is conducted while the film is moved at a rate of 4-900 ft./min.

24. "Orienting Poly(ethylene terephthalate) Films"
Brit 850,993

Biaxially oriented films with a birefringence of less than 0.03 are produced by first stretching in one direction, then determining and controlling the work input required to give optimum stretching in the other direction.

25. Yukio Ito
"Permeability of High Polymer Films to Gases and Vapors. IX. Permeability of Stretched and Oriented Polymer Films"
Kobunshi Kagaku 18, 6-12 (1961)

The permeability of some stretched and oriented polymer films to gases and water vapors was examined. The permeability coefficient (P) decreases with the increase of orientation.

26. Yoshio Iwamura
"Polyester-urethan Block Copolymers"
Japan 17,596 ('60)

A mixture of 10 grams poly(ethylene terephthalate) (acid value 0, OH value 40.3) and 100 cc nitrobenzene is stirred at 170°. Then a solution of 1.2 gram tetramethylene diisocyanate in 10 cc of nitrobenzene is added, and heated at 160-170° for 4 hours. Workup gives 17.5 g. of a colorless plastic powder.

27. Yoshio Iwakura, Yasud Taneda
"Preparation and Property of Polyester-Urethan Block Copolymers"
J. Appl. Polymer Sci. 5, 108-15 (1961)

A urethan block copolymer of poly(ethylene terephthalate) (I) and poly(ethylene adipate) (II) were obtained. Elastic properties were observed in some of the block polymers containing 15-50% of (I). Thus, the 15/85 (I)/(II) composition has a tensile strength of 240 kg/sq.cm. and 700% elongation.

28. Gerald Oster
"Grafting of Monomers to Hydrogen-Containing High Molecular Weight Materials"
Brit 856,884

A high molecular weight polymer having hydrogen atoms in its molecules is treated with an activator, i.e., benzophenone, capable of absorbing ultraviolet light with wave lengths of 170-300 mu. When exposed to this ultraviolet light, the polymer is converted to a free radical form and will copolymerize with materials containing ethylenic double bonds.

29. Ichitaru Uematsu and Yoshiko Uematsu
"Effect of Crystallinity on the Physical Properties of High Polymers"
Kobunshi Kagaku 17, 222-6 (1960)

The effect of crystallinity on the glass transition temperature, Tg, and on the volume expansion coefficient of poly(ethylene terephthalate) films are determined by measurements at 25-98°. The crystallinity of the films was successively changed by heating them at 120, 150, 210, and 238°. For the samples crystallized at low temperatures, Tg shifts rapidly to higher temperatures.

1960

30. C. P. Fortner
"Oriented Thermoplastic Sheet and Film"
Materials in Design Engr. 40, No. 7, 94-99 (1954)

Biaxial orientation by stretching a material to line up the molecules changes the properties, particularly mechanical strength and toughness.

Oriented thermoplastics discussed include polystyrenes, acrylics, polyesters, sarans, polyethylenes, polypropylenes, rubber hydrochloride and others such as poly carbonates, rigid vinyls, nylon, and fluorocarbon films. Properties of unoriented and biaxially oriented thermoplastics sheets are discussed.

31. J. L. Murphy (Monsanto)
"Thermo-forming Biaxially Oriented Film and Sheet"
Plastics Technol. 5, No. 10, 42-4 (1959)

Dominant variables that contribute to improper vacuum forming of oriented sheet and film are known to include sheet clamping, heat equalization, mold temperature, cycle timing, drape and adequate vacuum. Variables in the forming operations are described, together with some of the recent forming equipment and product design.

32. D. A. Barr, R. N. Haszeldine and C. J. Willis
"New Elastomers Containing Fluorine"
Proc. Chem. Soc. 1959, 230

In the reaction of trifluoro nitroso methane with tetrafluoro ethylene, use of carefully purified monomers, a reactant ratio close to 1:1, and temperature of 0° or below, enables an elastomer to be obtained directly and quantitatively which is stable at 200° in air and is flexible at -30°. Molecular weight is 150,000 - 200,000, and it is insoluble in all common solvents. Other comonomers may be used instead of tetrafluoroethylene.

33. W. P. Slichter (Bell Labs)
"Study of High Polymers by Nuclear Magnetic Resonance"
Fortschr. Hochpolymer-Forsch. (J.D. Ferry et. al., editors, Springer-Verlog) I, No. 1, 35-74

33. (a) A. E. Woodward and J. A. Sauer
"Dynamic Mechanical Properties of High Polymers at Low Temperatures" ibid. 114-58.

34. H. Klumb and R. Dauscher
"Passage of Gases Thru Plastic Films"
Vakuum-teck 7, 35-41 (1958)

Films of Mylar (0.004 cm), Mipolar (0.055 cm) and Hostaphane (0.004 cm) are investigated as to permeability for H, He, O, and N. A graph depicts the temperature dependence of the permeation.

35. R. S. Barton
"Permeability of some Plastic Materials to H, He, N, O and Ar"
(Atomic Energy Research Estab.)(Great Britain) M599,4pp (1960)

The permeability in cc at NP x cm^{-2} (thick) X sec^{-1} x cm^{-1} Hg measured at $23^{\circ} \pm 1^{\circ}$ was:

	H	He	N	O	Ar
Polythene	$1x10^{-9}$	$7x10^{-10}$	$1.2x10^{-10}$	$3.6x10^{-10}$	$3.3x10^{-10}$
Polytetrafluoro-ethylene	$2.4x10^{-9}$	$7x10^{-8}$	$3.1x10^{-10}$	$1x10^{-9}$	$5.8x10^{-10}$
Perspex	$3.3x10^{-10}$	$7x10^{-10}$	below $1x10^{-11}$	below $1x10^{-11}$	$1x10^{-11}$
Nylon 31	$1.6x10^{-11}$	$3.7x10^{-11}$	$1x10^{-11}$	$1x10^{-11}$	$1x10^{-11}$
Nylon 51	$6.3x10^{-11}$	$1.1x10^{-10}$	$1x10^{-11}$	$1x10^{-11}$	$1x10^{-11}$
Poly(vinyl toluene)	$2.0x10^{-9}$	$1.8x10^{-9}$	$7.7x10^{-11}$	$1x10^{-11}$	$1x10^{-11}$
Polystyrene	$1.6x10^{-9}$	$1.6x10^{-9}$	$6.3x10^{-11}$	$1x10^{-11}$	$1x10^{-11}$

36. J. Herscouiw, B. H. Leuca and R. Mihail
"Grafting of Polycondensates Under the Action of Ionizing Radiation"
Proc. U.N. Intern. Conf. Peaceful Uses At. Energy. 2nd. Geneva, 1958 29, 201-5 (1959)

Films of poly(ethylene terephthalate) and poly caprolactam were irradiated with X-rays, and a Co^{60} source in solutions of acrylonitrile, methyl methacrylate and styrene at doses of approximately 1.5×10^6 rad. Conditions most favorable to grafting and the properties of the grafted films are described.

37. V. V. Korshak, K. K. Mozgova, and M. A. Shkolina
"Preparation of Graft Copolymers V. Grafts of Vinyl Monomers on poly(ethylene terephthalate)"
Vysokomolekulyarnye Soedineniva I, 1604-9

Films or fibers of poly(ethylene terephthalate) were treated with O_3 for 5 minutes, then heated in $PhCH{:}CH_2$(I) for 10 minutes, then boiled with C_6H_6, and dried. Increases in weight of 53% and 40% for film and fiber respectively were obtained. The suggested mechanism is formation of hydroperoxide by attack at CH group, decomposition of this to RO. radical, and combination with (I) to give $RO(CH_2CHPh)_n$.

Relative elongation of before and after copolymerization are: 192.7,280; tensile strength (kg/sq.cm.) 1552,876.4; thickness 19-20μ 32-38μ.

38. "Graft Polymerization"
Fr. 1,181,813

Monomers are grafted onto solid polymers by irradiating the polymers in contact with the monomer vapor. CH_2: CHOAc on poly(ethylene terephthalate).

39. M. Wick
"Boron Siloxane Polymers"
Kunstoffe, 50 433-6 (1960)

Organo silicone polymers are surveyed. Bouncing putties are discussed, which are dimethyl poly siloxanes having a Si-O-B bond. It was further observed that homogeneous adhesions could be obtained from dimethyl polysiloxanes (Mol. wt. 400,000) with approximately 30% boron nitride, Boron Containing Siloxanes (Mol. wt. 350,000 - 500,000) can be crosslinked via peroxides into nontacky elastic materials.

1959

40. S. Rosenbaum (Brooklyn Polytech)
"Block Copolymers of Poly (ethylene terephthalate)"
Univ. Microfilms (Ann Arbor, Mich) L. C. Card No. MIC 58-2877, 95 pp., dissertation abstract. 19,675 (1958)

41. Otto E. Van Luhulzow, Eric Moulton and Ferdinand Schouteden
Poly(ethylene terephthalate)
U.S. 2,867,650, Brit. 804,495, Belg 542,060
(to Gevaert Photo-Producten V.V.)

42. William Holmes-Walker, John F. E. Adams and Kenneth G. Gerber
"Biaxially Oriented Thermoplastic Films, Especially Poly(Ethylene Terephthalate)"
Brit 811,066 (to Imperial Chemical Ltd.)

Films of high tensile strength were produced by drawing in two directions at right angles with heating. The film may be used for a variety of uses such as recording, packaging, etc. For example, flat amorphous poly(ethylene terephthalate) film is drawn forwards over a heated roll to a ratio of 2.5:1 at 5 ft./min. at 85°; then sideways at a 3.25:1 ratio in a water bath at 85° and 10 ft./min, and finally at a 2.25:1 ratio over a roll at 150° and 5 ft./min.

43. A. H. Wilbourn
"Glass Transition in Polymers with the $(CH_2)_n$ Group"
Trans. Faraday Soc. 54, 717-29

The glass transition temperature (Tg) is defined in molecular terms as the point where the main polymer chain acquires large scale mobility. Transitions at lower temperatures were attributed to the acquisition of limited mobility by portions of the main chain or by side groups. Incipient crystallization temperature was used for determining the Tg of crystalline polymers. The mechanical dynamic behavior of polymers containing $(CH_2)_n$ (poly(alkyl methacrylates), linear and branched polymethylenes, polythenes, poly(α-olefins), linear polyethers, and 6,6-nylon) is interpreted on this

basis. A minimum $(CH_2)_n$ is required for the characteristic transition at about -120°. Effects of y-branch points in a carbon-carbon chain are considered.

1958

44. J. S. Rugg and A. C. Stevenson
"Viton-A, A New Fluorine-Containing Rubber"
Rubber Age 82, 102-4

Viton-A, a linear copolymer of vinylidine fluoride and hexafluoro propylene contains approximately 65% Fl, has a specific gravity of 1.85, Mooney viscosity 35-45, and relatively low molecular weight. Properties of a typical sample: 2375 lbs/sq.in. tensile strength, 300 lbs/sq.in. modulus at 100% E, 350% elongation, 66 Shore A hardness, 43% resilence, 25% set, -47°F Brittle Point. Resistance to O_2, O_3 and weather is excellent. Plasticizers improve low temperature properties.

45. D. S. Ballantine, P. Columbo, A. Glinex, B. Manowitz and D. J. Metz (Brookhaven)
"Fission Product Utilization IX. Radiation Induced Graft Copolymerzation and Solid State Polymerization"
U.S. Atomic Energy Comm. BWL 414 (T-81)

Graft copolymers have been prepared by irradiation of the following systems by Co^{60} γ-rays (all polymers in the shape of films). Polyethylene immersed in styrene monomer, polyethylene in acrylonitrile, polyethylene in 4-vinyl pyridine; polyethylene in methyl methacrylate; teflon in styrene or in N-vinylpyrolidone (20% aqueous solution) respectively. Furthermore, the systems, Teflon-acrylonitrile, Teflon-vinyl acetate, Hevea-styrene, Hevea-acrylonitrile, dimethyl silicone rubber - acrylonitrile, Mylar-styrene, polypropylene-styrene, and Nylon-styrene have been considered. Incomplete studies indicate that the graft is chemically bound to the original polymer. Previously reported solid state polymerizations data are summarized.

46. Dudley B. Chelton and Douglas B. Mann
"Cryogenic Data Book" (NBS, Colo)
U.S. Atomic Energy Comm UCRL-3421, 116 pp (1956)

47. J. A. Meyer, C. Rogers, V. Stannett, and M. Szwarc.
"Gas and Vapor Permeability of Plastic Films and Coated Papers"
Tappi 40, 142-6 (1957)

The permeability constants of a number of plastic films such as polyethylene (I), Mylar (II), and nylon, have been measured for N, O, and He with a specially designed apparatus.

48. Francis P. Alles
"Polyester Films"
U.S. 2,779,684 (duPont)

For better dimensional stability, films of polymeric esters of dicarboxylic acids and dihydric alcohols, such as poly(ethylene terephthalate), which were oriented biaxially and heat set at 150-210° under tension, are reheated at 110-50° for 1-5 minutes under a tension of 10-25 lbs/sq.in.

1957

49. R. J. Corrovini (NBS, Boulder)
"Properties of Materials at Low Temperature"
Chem. Engr. Progr. 53, 262-7 (1957)

This review summarizes the knowledge acquired from work at the Boulder laboratory on low temperature data, organized and interpreted in the light of theory and shows how useful estimation procedures can sometimes be derived from theory to fill gaps in available data.

APPENDIX B

BROAD-LINE NMR APPARATUS

APPENDIX B

BROAD-LINE NMR APPARATUS

Broad-Line NMR Apparatus

If a sample is placed in an appropriate magnetic field, application of a radiation field of the proper frequency will cause the sample to absorb energy. The resonant frequency for nuclear spin transitions is of the order of 1-40 mcps in fields of <10,000 gauss. This is in the range of radio frequencies and the techniques used therefore are similar to those employed in commercial radio work. The particular technique used in this work involves placing the sample in a coil which is used as the inductive component of the tuning network of an oscillator. Sample and coil are then placed in the magnet gap, and as an oscillator frequency is varied through the resonant frequency of the nuclei, energy is absorbed, the oscillation level drops, and the change in level is detected and amplified. Amplification and detection are greatly simplified through use of a modulation system which entails superposition of a low audio frequency component on the fixed external magnetic field. This modulation causes the nuclear resonant frequency to vary at an audio frequency rate. Thus the sample goes in and out of resonance at this same rate, and the signal may then be amplified by standard radio and audio frequency techniques rather than by dc amplification which is difficult and unstable in operation.

The block diagram of the apparatus is shown in figure B-1. The r-f unit contains the oscillator with its motor-driven tuning capacitor, and several stages of amplification. The audio output is fed to the tuned amplifier which eliminates all frequencies except those directly caused by the sample, which of course varies at the modulation frequency. In all the experiments of this work, the modulation amplitude was set to a fraction of the line width so the amplitude of the signal is determined by the slope of the line at the frequency determined by the oscillator. The signal is fed to the phase-sensitive detector which, when synchronized by a signal from the modulator unit, sends a dc signal to the recorder which is proportional to the first derivative of the absorption line intensity.

The actual circuits of all the units in figure B-1 are based on circuits supplied by Watkins and Pound.[1] [2] [3] Several adaptations to our purposes were made at the time the oscillator, modulator, and phase-sensitive detector were constructed, and several improvements suggested themselves during the course of the work.[4]

1. R. V. Pound, Rev. Sci. Inst., 21, 219 (1950).
2. G. D. Watkins, Thesis, An RF Spectrometer with Application to Studies of Nuclear Magnetic Resonance Absorption in Solids, Harvard, 1952.
3. G. D. Watkins, private communications.
4. Full details of the circuits and their operation are given in the Harvard thesis, ref. 9, and in ONR report N5-ori-07661.

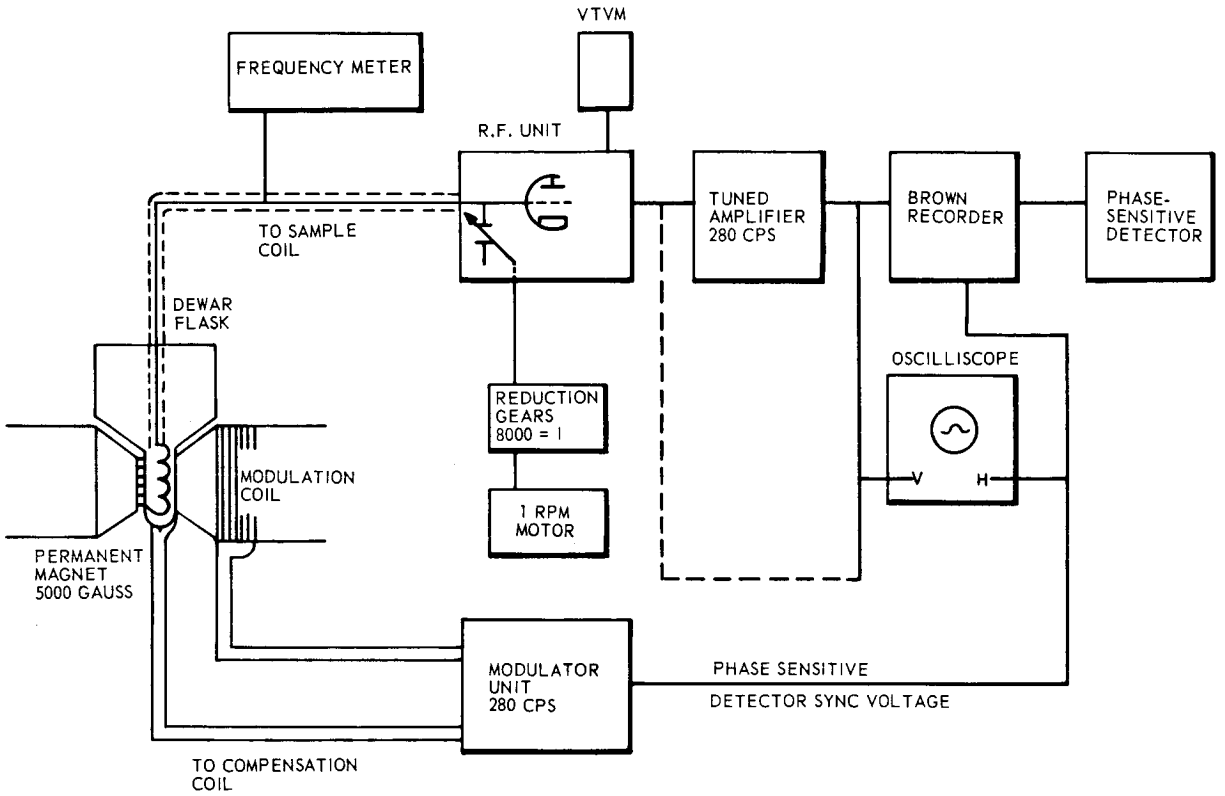


Figure B-1. Block Diagram of Apparatus

The design of the magnet was influenced in part by the materials on hand. A yoke was constructed of two soft iron bars 4 x 7 x 27 inches and two 4 x 7 x 20 inches ground flat at the bolted joints. Several discs of Alnico V, each one inch thick and six inches in diameter,[5] were assembled to form either pole, and these were secured by a stainless steel bolt to the yoke and to the soft iron pole pieces four inches in diameter. The Alnico was magnetized by a current of 100 amperes through a pair of specially wound coils which later were used as the modulation coils. A permanent field of 5,050 gauss was obtained within the gap of 1-4 inches, with an inhomogeneity of 0.3 gauss over a sample one inch long.[6]

A cryostat was necessary for the observations at low temperature, and this was built in the form of a Dewar vessel 8 inches in diameter at the top and tapering to a tubular section 1.25 inches in diameter at the lower end. The tubular section extended into the magnet gap, and the sample within its sample coil extended down into the magnetic field within a closed-end glass tube within the Dewar vessel. Temperatures were measured by means of a thermocouple extending through the cork of the sample vial and into the sample. The cryostat was filled directly with liquid nitrogen or with a mixture of acetone and dry ice, since the cooling liquid did not come into contact with the sample coil or vial. Measurement at temperatures other than 77°K and 193°K were attained by cooling the cryostat below the desired temperature and allowing it to warm slowly; the heat capacity was sufficient to allow scanning the absorption line in this manner.

The general procedure in examining a sample was to adjust the oscillator frequency until the absorption line could be observed on the oscilloscope, adjust the modulation level, compensation, and phasing controls, and then sweep through the line by means of the motor-driven oscillator tuning capacitor shown on the block diagram. The signal was then recorded as unbalance in the output push-pull stage of the phase-sensitive detector on the specially adapted recording potentiometer. The recorded curves were smoothed by drawing a line through the mean points of the fluctuations, and the horizontal scale converted from cycles per second at fixed magnetic field to variation of gauss at fixed frequency in order to conform with the conventions of published work.

Improvements

The success of the broadline NMR method in explaining the properties of silicones, as published in the first volume of the Journal of Inorganic and Nuclear Chemistry, pp. 92-111 (1955), led to application of the same

5. The authors are indebted to the Carboloy Department of the General Electric Company for the loan of the Alnico at a time when it was not available without priorities and long delays.

6. It should be emphasized that the objective of the present investigation was the determination of line widths ranging from five to twenty-five gauss or more, and so high resolution was neither necessary nor desirable. The same magnet would probably not do for chemical shift work, and a new one of greater field homogeneity is being constructed for such work.

method to the study of organometallic polymers of germanium and tin, to the study of ferrocene and its derivatives, and to polyethylene, fluorocarbon polymers and the like. Each time the instrument was required to do something new and different it became necessary to effect considerable adjustment. A new permanent magnet was bought to replace the home-built one that was in use, the circuits were rebuilt and improved, a new power line was installed to eliminate interferences, and the experimental method was gradually refined. These improvements are described in the technical report on Contract No. Nonr-1866(13), to the Chemistry Branch of the Office of Naval Research in February, 1962, entitled, "Improvement of a Broadline Nuclear Magnetic Resonant Spectrometer", by Gerhard Englert and Richard Volpicelli.

It should be emphasized that in the methyl silicone polymers the structural components which are doing almost all of the moving are the methyl groups, and these, in effect, are side groups which are not part of the structural chain. Hence the methyl groups are free to move rather readily even though the structural backbone or polymeric chain is not flexing through the influence of thermal agitation. In a polymer like polyethylene the only proton-containing segments are actually part of the polymeric backbone, and hence these hydrogen atoms can move only if the backbone itself is flexing. There is considerably less freedom for motion within the backbone, and therefore the instrument had to be made much more sensitive in order to examine polyethylene. When the first samples of Mylar were received, it was obvious that another major increase in sensitivity was required, simply because the hydrogen content of Mylar is much less than that of polyethylene and because the degree of motion was also much less in this characteristically stiff and rather crystalline polymer. Two major changes in the equipment were necessary.

1. Because the output of the detector and amplifier is filtered by a highly-tuned filter, set exactly for 280 cycles per second, any deviation of the modulation frequency from 280 cycles leads to loss of signal and hence loss of sensitivity. The vacuum tube oscillator which produced the 280 cycle note had been known to vary slightly with time and temperature, but the effect was not important as long as the absorption lines were of large amplitude and not much sensitivity was required. We now needed all of the sensitivity we could get, and more. For this reason the vacuum tube oscillator was removed and a new 280 cycle oscillator was devised which is controlled by an electrically driven tuning fork which maintains a frequency of exactly 280 cycles. This improved matters considerably, and it was possible to get room temperature spectra for all of the polymer samples sent in between June 1 and September 1, 1964.

2. In attempting to get spectra at low temperatures for the polymers of interest, it became evident that the absorption lines were not symmetrical and that the zero line drifted considerably. After exhaustive tests it was found that the power amplifier, that was being used to modulate the

magnetic field 280 times per second, was incapable of swinging the massive iron pole pieces of the magnet sufficiently to get the large amplitudes we required. For this reason a new power amplifier was constructed that was capable of 60 watts output; it was installed in place of the old one. The result was an improvement, but operations are still at the ragged edge of sensitivity of the instrument.

At this point the instrument was capable of examining all of the recent samples of synthetic polyesters which had come in, and spectra for such polymers from 77°K up to and beyond room temperature could be obtained. However, at the same time the changes in the instrument described above were being made, emphasis within the project began to shift to properties of the polymers at 20°K. There was no way of attaining a minimum temperature of 20°K except through the use of liquid helium. In order to use liquid helium it became necessary to replace the entire cryostat, modulating system, and sample container, with a modified assembly capable of transferring liquid helium to the sample and maintaining a temperature not at the boiling point of liquid helium (4°K) but 16°K higher. Any conceivable device would require that the sample be surrounded not only with a stream of very cold helium, but also that the helium stream be encased in a jacket of liquid nitrogen and the body of liquid nitrogen within a vacuum jacket or Dewar vessel. Since only 1.5 inches were available between the fixed pole pieces of the permanent magnet, it became necessary to do away with the Helmholtz coils formerly used for modulation within the magnetic gap in order to make room for the eight layers of glass and the spaces between them required for the vacuum jacket, the liquid nitrogen layer, and the cold helium layer. Before building such a complicated device, it became necessary to find out how the magnetic field could be modulated without using the bulky Helmholtz coils. In November 1964, the entire instrument was modified to install a system of frequency modulation which had been tried out for a different purpose in the Harvard Laboratories; a system which would not require the Helmholtz coils but would apply the 280 cycle modulation to the radio frequency sample coil by a true process of frequency modulation. Fortunately all of the circuits could be borrowed and things were set up on a temporary basis. The results were very disappointing; the zero line drifted, the amplitude and sensitivity were insufficient, and the spectra generally unacceptable. Everything possible was considered, and it was concluded that a long period of development of new circuits and methods was necessary for use of frequency modulation in the instrument. Since neither the time nor the money for such extensive development was available, the instrument was put back together the way it was, the studies at 77°K and above were continued.

Some of the equipments used in this study are shown in figures B-2 through B-8.

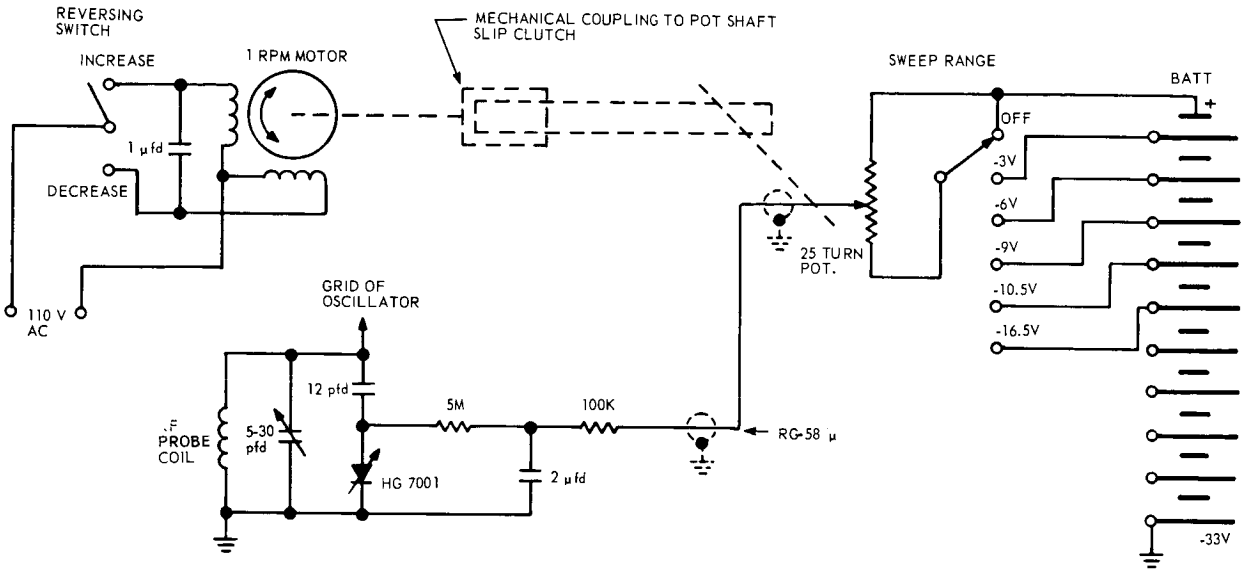


Figure B-3. Remote R-F Scanning Circuit

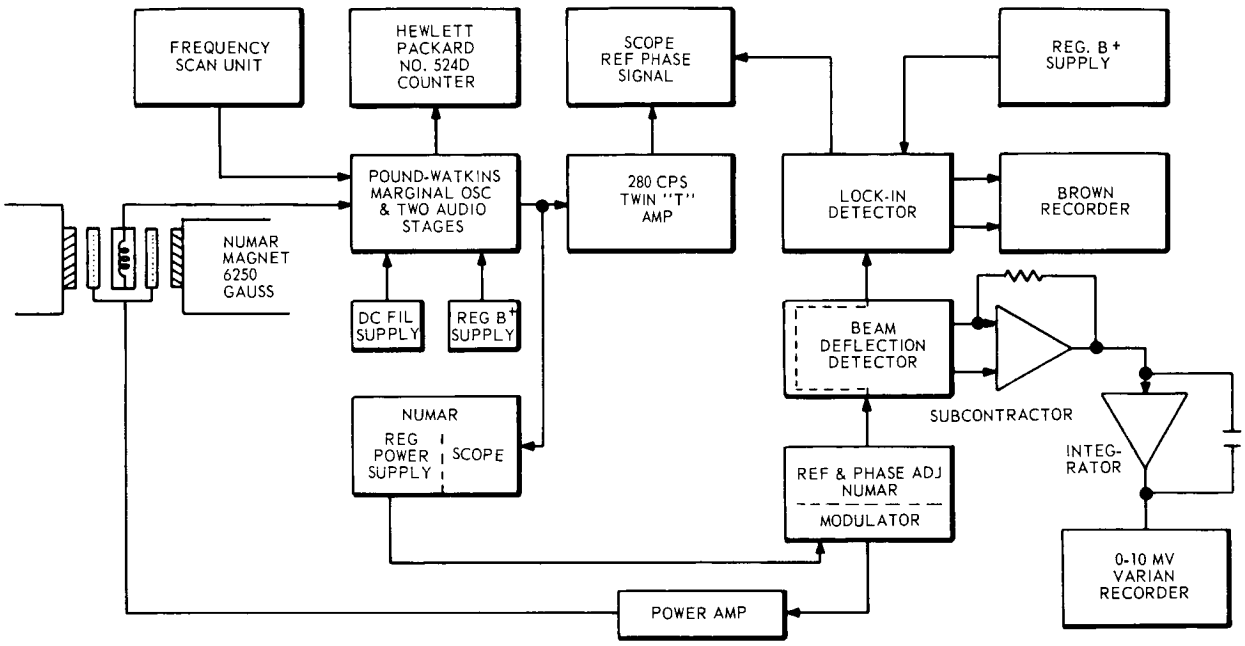


Figure B-2. Block Diagram of Broad-Line NMR Spectrometer

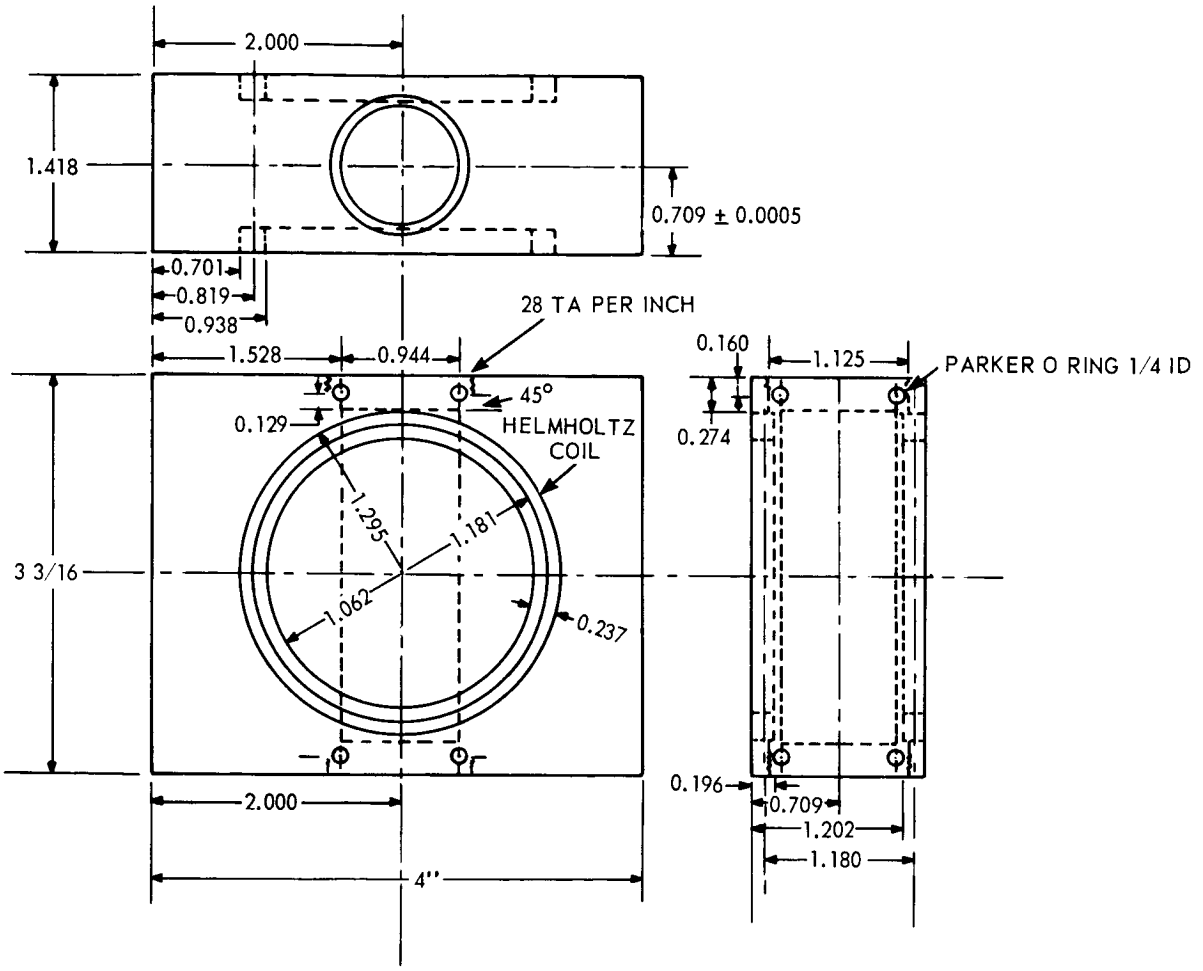


Figure B-4. Helmholtz Coil and Probe Assembly

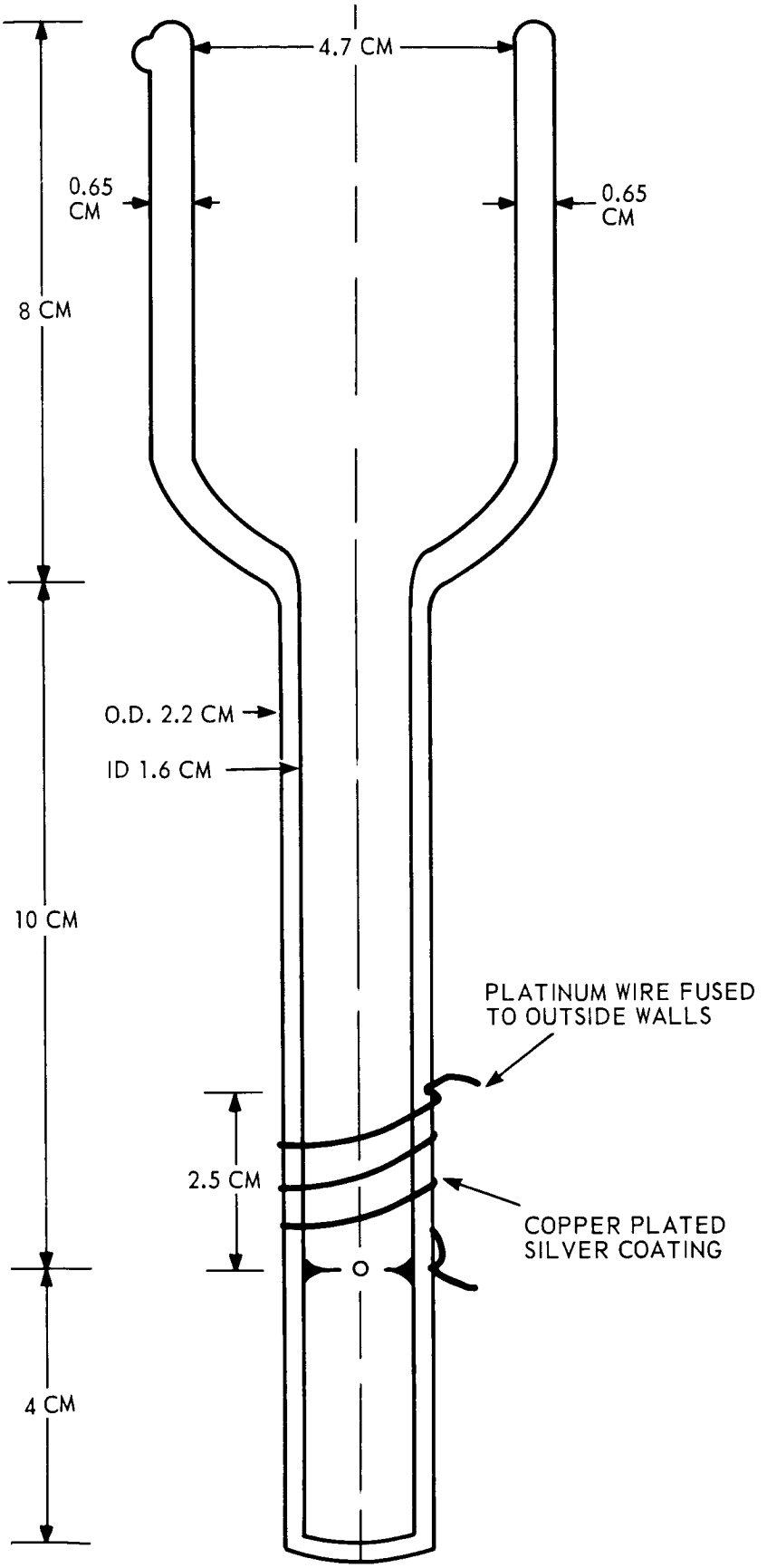


Figure B-5. Liquid Nitrogen Dewar

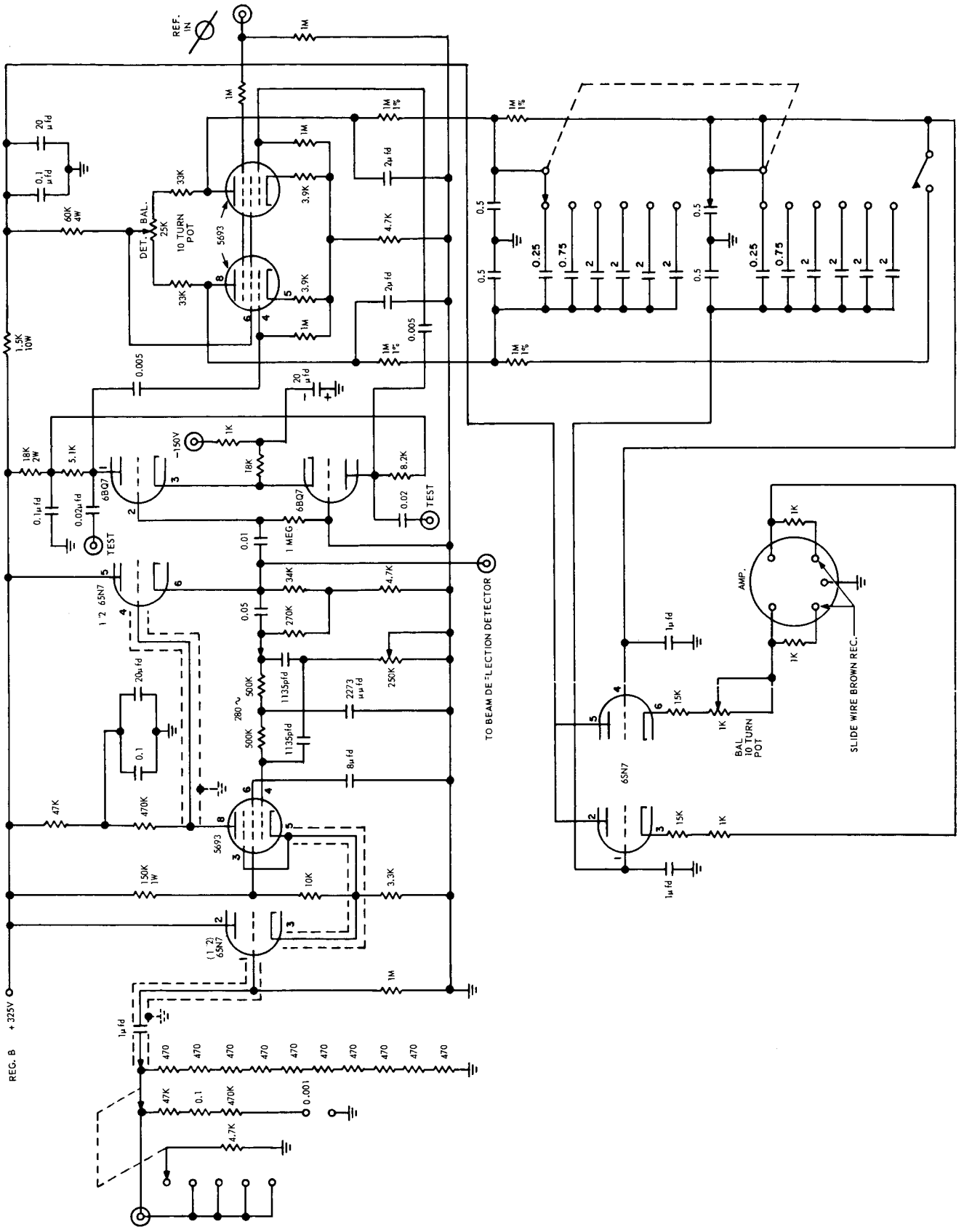


Figure B-6. Modified Lock-in Amplifier and Detector

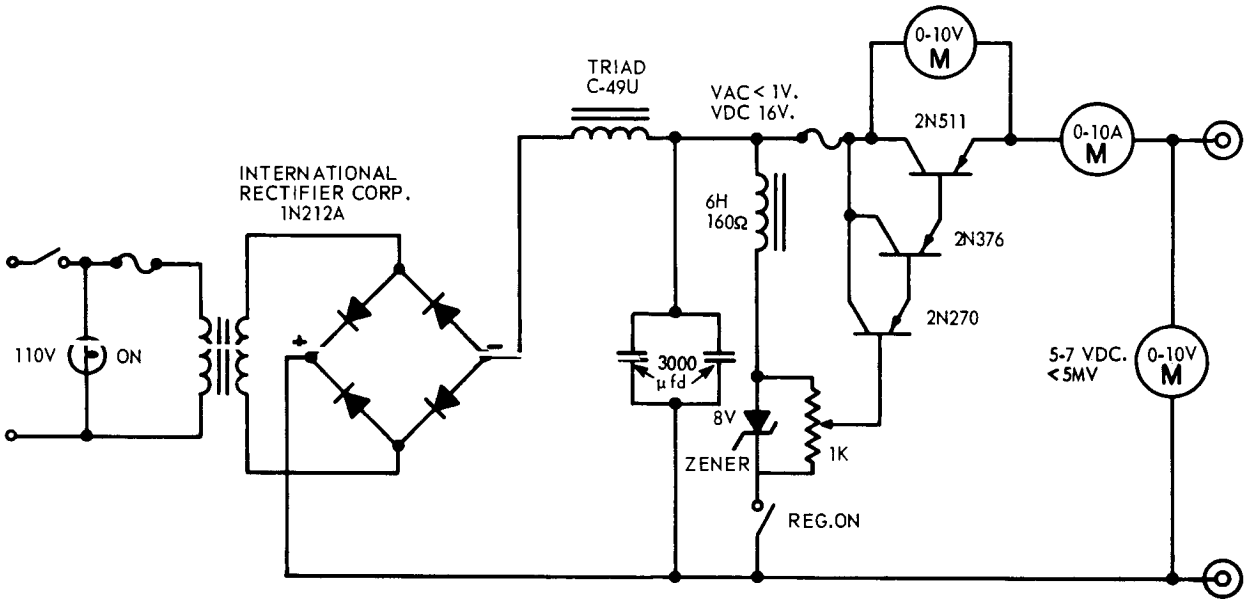


Figure B-7. Regulated DC Fil. Supply

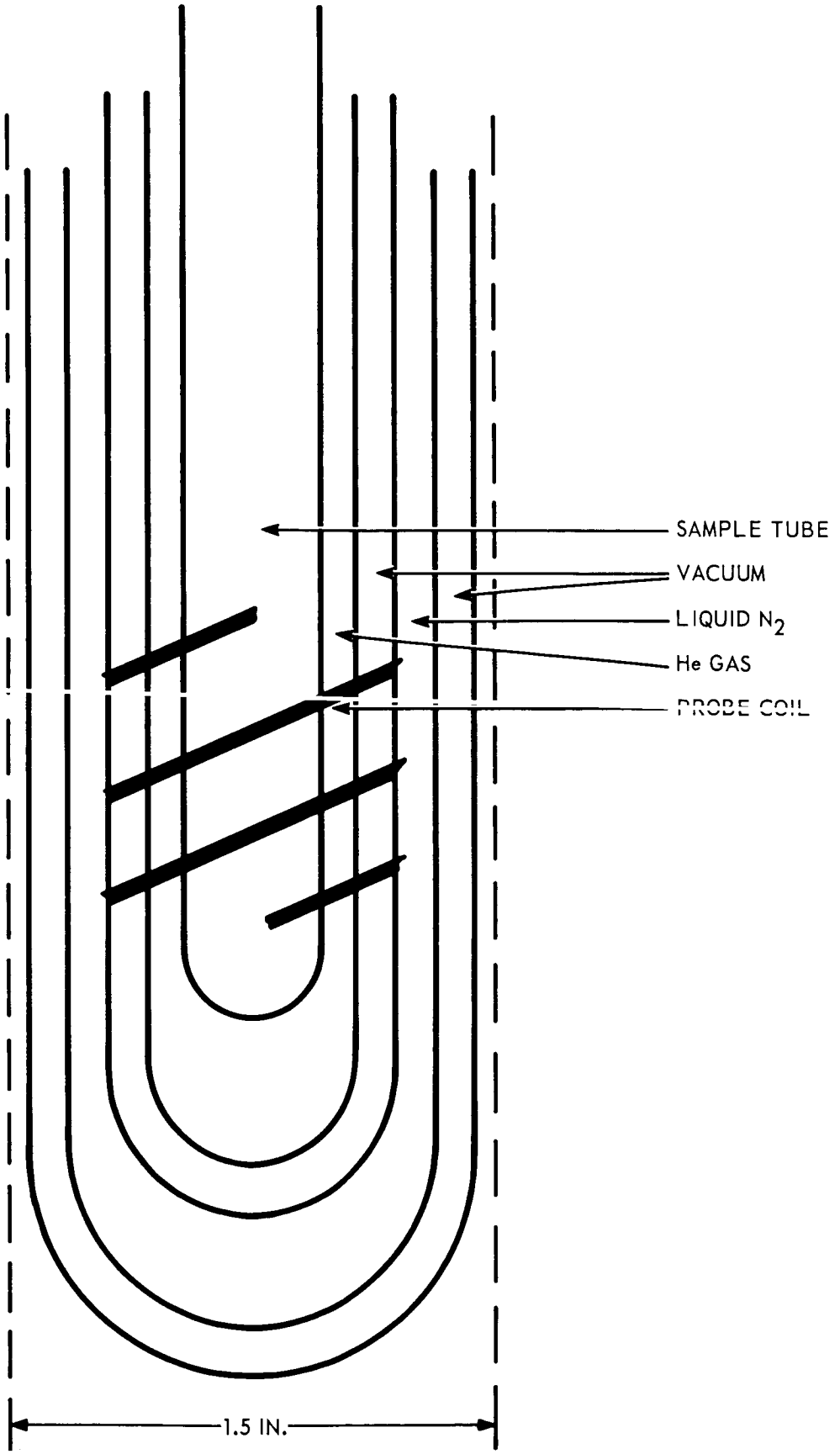


Figure B-8. NMR Cell

APPENDIX C

MEETINGS WITH CONSULTANTS

APPENDIX C

MEETINGS WITH CONSULTANTS

Meeting with Dr. H. C. Brown

On 20 May 1964, a meeting was held at Melpar with Dr. H. C. Brown, of the University of Florida, to discuss the potential of fluorinated polymers for use in expulsion bladders and liners at cryogenic temperatures.

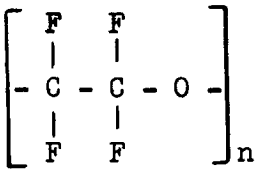
The following comments were made by Dr. Brown:

1. Fluorocarbon polymers consisting only of carbon in the backbone would not be expected to be very flexible at cryogenic temperatures. Their use might therefore be limited only to liners. They might however prove useful in expulsion bladders in conjunction with another polymer which is flexible at cryogenic temperatures, e.g., when grafted on to a more flexible polymer.

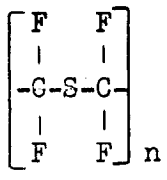
2. Fluorinated polymers, in general, appear to exhibit unique oxidative stability (to LOX at cryogenic temperatures). Accordingly, their use in bladders and/or liners for LOX should be seriously considered.

3. The following fluorinated polymers appear to be more flexible than the fluorocarbons, based on various reports, and should be considered in this program.

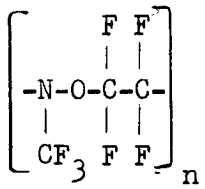
a. Perfluoroethers, e.g.,



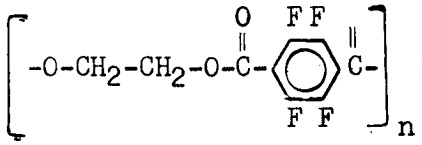
b. Perfluorothioethers, e.g.,

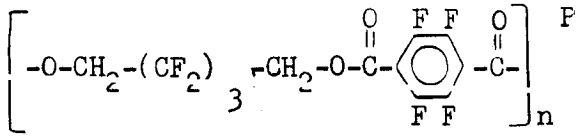


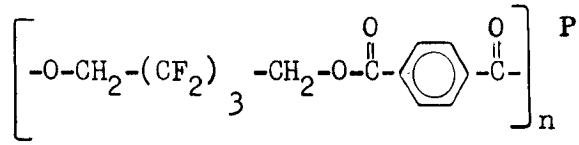
c. Nitrosorubbers, e.g.,



4. The following fluorinated modifications of polyesters might be of interest:

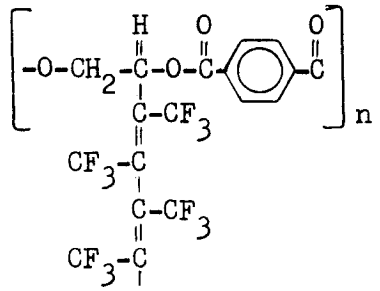
a.  Poly(ethylene tetrafluoroterephthalate)

b.  Poly(2,2,3,3,4,4-hexafluoro-pentamethylene tetrafluoro-terephthalate)

c.  Poly(2,2,3,3,4,4-hexafluoro-pentamethylene terephthalate)

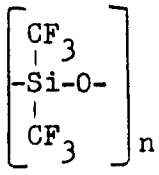
The starting fluorinated terephthalic acid and glycols are well known and may be commercially available. When asked about the possible direct fluorination of Mylar, Dr. Brown stated that this would probably be very difficult to achieve.

5. The ease at which perfluorobutyne-2 undergoes polymerization, e.g., under low energy γ-radiation, suggests its use for grafting on to another more flexible polymer (for improving the latter's compatibility with LOX). Thus Mylar might be contacted with perfluorobutyne-2 in the presence of γ-radiation to produce the following graft co-polymer.



6. Dr. Brown has observed that when Teflon powder is heated with sulfur in air it is converted to a waxy soluble polymer possessing the same first order transition, Tm-327°C as the starting Teflon. He did not attempt to cast films from this material.

7. Dr. Brown predicted that a perfluorinated dimethylsilicone, such as the following should be highly "unstable".



He believed that such a material would not be stable even at room temperature.

8. Dr. Brown emphasized that there was really no good reason why fluorinated polymers in general should be ruled out for use in expulsion bladders, since fluorocarbons, per se, are no more representative of the many possibilities available for fluorinated polymers than are polyethylene type polymers representative of all other hydrocarbon type polymers. On the other hand, when he was queried about the utility of polyvinyl fluoride, polytrifluorochloroethylene and poly-perfluoroisobutylene, he suggested that heteropolymers containing fluorine appendages should be more suitable. Dr. Brown suggested that Melpar consider the use of certain fluorinated butadiene polymers, previously studied at the Quartermaster Corps.

Dr. Serafini of NASA-Lewis noted that Dr. Brenner and his coworkers at N.Y.U. have reportedly obtained impermeable, thin films of Teflon by subjecting tetrafluoroethylene (in the gas phase) to an electric discharge. The point here is that certain gas phase polymerization processes may provide known polymers in new and possibly more useful forms.

Dr. Brown agreed to submit a list of the fluorinated polymers he considered to have the greatest potential for the intended applications.

Additional Suggestions Obtained from Dr. Brown

Listed below is a list of fluorinated polymers Dr. Brown considers to have potential for this program and references to their preparation or source.

1. Copolymers of 1,1,2 and 1,1,3-trifluorobutadiene
   (Dr. J. C. Montermoso, Quartermaster Corps)

2. Vinylidene Fluoride - CTFE Copolymer
   (Kel F type 3700)

3. Vinylidene Fluoride - Perfluoropropene Copolymer
(Viton, Fluorel)

4. Poly (fluoroalkyl) acrylate
(3M Products 1F4 or 2F4)

5. Fluoropolyesters
(Hooker Chemical Co. prepared various polymers of this type using $HO-CH_2-(CF_2)n-CH_2-OH$ and either conventional or fluorinated diacids for the Air Force)

6. Silastic LS-63
(Dow Corning, Midland, Mich.)

7. Fluorocarbon Nitroso Rubbers - originally a copolymer of CF_3NO and C_2F_4
(Reaction Motors Div., Thiokol Chemical Co.)

8. Nitroso Rubber

$$\left[-N(-X)-O-CF_2-CF_2-\right]_n$$

X - NO_2, CL, etc.

(Dr. Crawford, 3M)

9. Fluoropolyethers

$$\left[-CF_2-CF_2-O-\right]_n$$

U.S. Pat. 3,125,599 (duPont)

10. Fluoropolysulfides

$$\left[-CF_2-S-CF_2-S-\right]_n$$

(duPont)

11. Plasticized Teflon or other fluorocarbons

MEETING WITH Dr. P. H. GEIL

On 27 August 1964 a meeting was held at Melpar with Dr. Phillip H. Geil of Case Institute of Technology to discuss the significance of polymer morphology in achieving flexible polymeric films at cryogenic temperatures.

The following comments were made by Dr. Geil:

1. The events that take place when a polymer film is biaxially oriented are not fully understood; however, extension of folds within a polymer crystal during stretching of the film could occur.

2. Sequential orientation in two directions as compared to simultaneous orientation in these directions could be expected to yield a polymer film with different "strength" properties.

3. Uniaxial orientation of a polymer might be expected to give a film with superior "strength" properties in the direction of orientation as compared to either direction of orientation in a biaxially oriented specimen.

4. Relative motion between molecules is a prerequisite for flexibility in polymers.

5. Motion within polymers as seen by broad-line NMR studies at cryogenic temperature should be directly relatable to polymer flexibility at these temperatures.

6. Another method of studying flexibility at cryogenic temperatures would involve the measuring of shear modulus and internal friction of a polymer system as a function of temperature. An apparatus that could be used for this purpose would be a dynamic viscoelastometer.

7. When asked about a possible explanation for the observed fact that Mylar is functional at liquid nitrogen temperature but fails at liquid hydrogen temperature, Dr. Geil said that the polymer probably goes through a transition point when cooled from liquid nitrogen to liquid hydrogen temperature and that some motion is thus frozen out below this transition temperature. He felt that this transition point would be detectable by broad-line NMR studies of Mylar over the temperature range specified.

8. Dr. Geil felt that a study of the effect of plasticizers on Mylar might prove of value for increasing flexibility at cryogenic temperatures. He cited a reference (Illers and Breuer, J. Colloid Sc., 18, 1-31 (1963) wherein the addition of 17-percent dioxane to a sample of Mylar, which was 28-percent crystalline, lowered Tg by 80°C, and, in addition, introduced a new transition at -180°C.

9. When asked what polymer system might be of value for this program, Dr. Geil replied that, since so little is known about polymer properties at cryogenic temperatures, it would be impossible to predict what polymer systems might have the desired properties at these temperatures. He felt, however, that studies directed at uncovering the reasons why Mylar "performed as well as it did" would be of more ultimate value in arriving at a solution to the problem.

10. In reference to flexibility within crystals, Dr. Geil was in agreement with our working hypothesis that motion within polymer crystals would occur at the defect areas within these crystals.

Dr. Geil left copies of seven articles that he felt were most pertinent for this program. He believed that these articles represent the current state of knowledge in the area of polymer morphology. The references to these articles are included below.

References Obtained from Dr. Geil

1. Heffelfinger, C. J. and Burton, R. L., "X-Ray Determination of the Crystallite Orientation Distributions of Polyethylene Terephthalate Films," Journal of Polymer Science, Vol XLVII, 289-306 (1960)

2. Illers, K. H. and Breuer, H., "Molecular Motions in Polyethylene Terephthalate," Journal of Colloid Science, 18, 1-31 (1963)

3. Schmidt, P. G., "Polyethylene Terephthalate Structural Studies," Journal of Polymer Science: Part A, Vol I, 1271-1292 (1963)

4. Kilian, H. G., Halboth, H., and Jenckel, E., "Rontgenographische Untersuehungen uber das Schmeltz-und Kristallisationsverhalten, vom Polyterephthalsaureglykolester(PTGE)," Kolloid-Zeitschrift, Band 172 Heft 2, 166-177 (1960)

5. Takayanagi, M., "Viscoelastic Properties of Crystalline Polymers," reprinted from the Memoirs of the Faculty of Engineering, Kyuschu University, Vol. XXIII, No. 1.

6. Sinnott, K. M., "Apparatus for the Measurement of Shear Modulus and Internal Friction between 4.2 and 100°K," Journal of Applied Physics, Vol 29, No. 10, 1433-1437, October 1958.

7. Jeschke, D. and Stuart, H. A., "The Diffusion and Permeation of Gases Through Polymers as a Function of Temperature and Degree of Crystallinity," translation from Zeitschrift fur Naturforschung, 16a, 37-50 (1961)

MEETING WITH PROF. C. SCHILDKNECHT

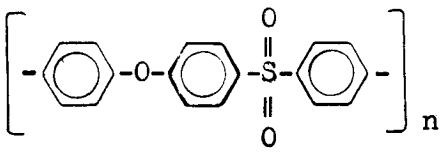
On December 10, 1964 a meeting was held at Melpar with Prof. C. Schildknecht of Gettysburg College, Gettysburg, Pa.

Prof. Schildknecht's polymer research has in recent years dealt with the synthesis and evaluation of a number of polyvinyl ethers. In discussing his work in this area he mentioned a recent finding that may have value in reducing film permeability to hydrogen. This discovery involves the partial cleavage of polyvinyl ethers with gaseous boron trifluoride to yield hydroxyl groups. This might be accomplished by either coating or grafting a polyvinyl ether onto a substrate film and then subjecting this film to gaseous boron trifluoride. This would cleave part of the pendant ether groups leaving

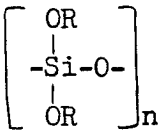
hydroxyl groups in their place. Mr. Marshall Cohen now at the University of Delaware could be contacted for additional details on this work.

Prof. Schildknecht indicated that samples of various polyvinyl ethers could be obtained by contacting Dr. Milton Friefeld or Dr. Eugene Hart at General Aniline and Film Corp.'s Central Research Laboratory, Easton, Pa.

Prof. Schildknecht mentioned several new polymers that might be of interest. These included a phenoxy sulfone:



from Union Carbide Corp. Also mentioned was an alkoxy siloxane:



which might be obtained by contacting Dr. John Wolfe, Head of Advanced Personnel, General Electric Co., Schenectady, New York.

Prof. Schildknecht indicated that it was his impression that Mylar contains some copolymer such as adipic and/or sebacic acid in it. On further questioning he said his information concerned Mylar as it was produced several years ago, and that it may be that Mylar no longer contains this added copolymer.

MEETING WITH DR. WM. SLICHTER

On Tuesday, March 30, 1965, a meeting was held with Dr. William Slichter of the Bell Telephone Research Laboratories, Murray Hill, New Jersey. Personnel present included Mr. R. F. Lark and Dr. T. Serafini of NASA-Lewis, Dr. R. Mattes of Harvard University, Mr. Z. Oser, Dr. J. M. Augl, and Dr. H. E. Podall of Melpar.

The following is a summary of some of the key points made by Dr. Slichter.

1. Broad-line NMR is of no value for assessing the "flexibility" of a polymer at cryogenic temperatures below Tg. (Dr. Slichter's views on the value of broad-line NMR for assessing polymer flexibility at cryogenic temperatures were in agreement with those expressed by Dr. Serafini at the 3rd Quarterly meeting for this program.)

2. The correlation of the line widths (at -195°C) and the twist-flex results of the polymer films thus far studied is probably fortuitous.

3. The term "mobility", applied to the reciprocal of the line width value, should not be used since line widths per se for a rigid lattice are not a measure of molecular motions. Below the temperature of line width narrowing (Tg) it is more correct to consider the line width as a measure simply of the proton packing within the lattice.

4. The extrapolation of such measurements from liquid N_2 to liquid H_2 temperature should in general not be erroneous since the lattice is already rigid, but such extrapolations are of little value here.

5. The NMR measurements should have been made to give the temperature of line width narrowing (T_β or T_g approximately and T_γ) rather than isolated line widths at only three temperatures. (Dr. Mattes has indicated that he has such data for some of the polymers studied to date.) However, even such information suffers from the same difficulty as the ranking of polymers on the basis of T_g.

6. A possible method to assess the flexibility of polymers would be to determine the characteristic frequency ν_c associated with the relaxation phenomena of various types of physical tests (involving different time scales for the relaxation measurements) and to plot the log of these values vs. the reciprocal of the absolute temperature at which the relaxation is measured. One could then rank the various polymers in terms of the slopes of the straight lines thus obtained; the slopes being a measure of the activation energy for relaxation of various molecular motions in the polymers.

7. Such a ranking of the polymers in terms of decreasing activation energies might be employed as a necessary but not sufficient condition for an increasing order of flexibility.

8. The difficulties of employing even such a method are:

a. The relationships of log ν_c vs. 1/T are generally not linear.

b. Extrapolations at high ν_c values to the low ν_c values, encountered in practice for the end mechanical property of interest, are dangerous.

9. For most reliable results (applicable to the end application) it is best to determine the performance of the polymer film in the true mechanical test of interest. Twist-flex at a single frequency, e.g., 9 cycles/min., which do not correspond to those encountered in practice may be dangerous. Twist-flexing at higher and lower frequencies encountered in practice is therefore desirable.

10. To obtain basic information relevant to the effect of polymer structure and morphology on flexibility at cryogenic temperature, Dr. Slichter suggested the use of a mechanical test which would measure the relaxation and stress-strain characteristics associated with, if possible, a single type of mechanical motion. Specific tests suggested for consideration include strain-creep relaxation, and biaxial deformation. Such measurements can be related more closely to corresponding motion on a molecular scale in a rigid polymer system (below T_g).